

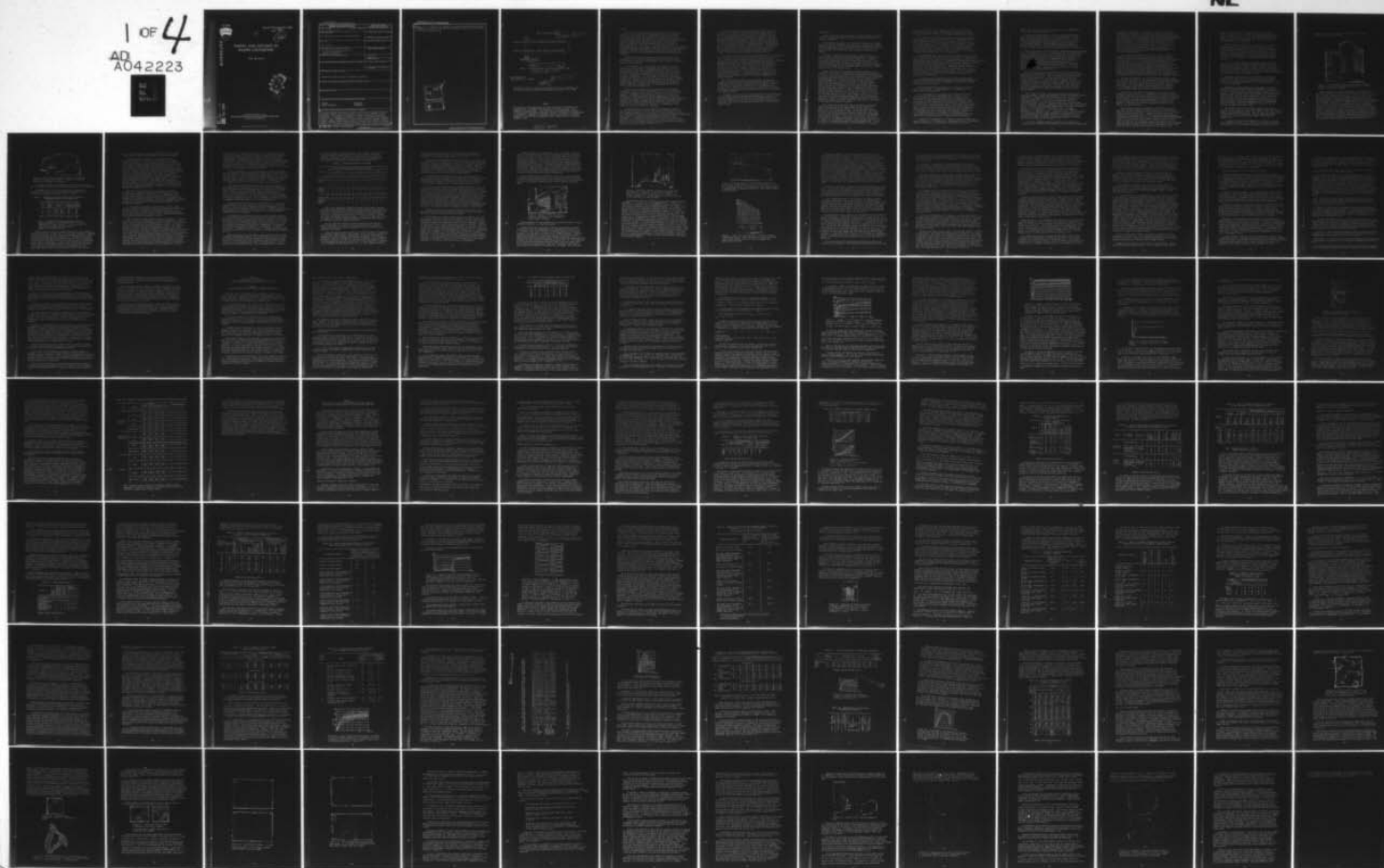
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THE THEORY AND METHODS OF WINTER CONCRETING (THEORIYA I METODY --ETC(U)  
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# THEORY AND METHODS OF WINTER CONCRETING

S.A. Mironov



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CORPS OF ENGINEERS, U.S. ARMY  
COLD REGIONS RESEARCH AND ENGINEERING LABORATORY  
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→ joints, etc.). This book is intended for researchers in scientific research institutes, construction laboratories and engineer personnel in construction and design organizations. ↑

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## Foreword

Almost 20 years have passed since the publication of the second edition of the book "The Theory and Methods of Winter Concreting". During this time a great deal has been accomplished in our country in developing the theory and technology of winter concrete, as well as in developing methods for carrying out concrete and reinforced concrete operations under winter conditions. During this time the use of precast concrete and reinforced concrete parts the year round has become very popular. The increase in cement quality, the use of fast-hardening concrete of better brands, the introduction of saline additives to produce concretes which harden in freezing weather and the preliminary heating of the mixtures are introducing significant changes into the technology of carrying out reinforced concrete operations under winter conditions.

On the basis of the systematization and generalization of the acquired data, the previously advanced ideas and hypotheses should now be partially replaced by the completely sound scientific viewpoints which have been acquired.

In the previous edition of the book, the problems of winter concreting theory were mainly associated with examining the role of the mineralogic composition of portland cement and the influence of technological factors on the properties of concrete mixtures and the physical and mechanical properties of the concrete which are cured at various temperatures. In this edition considerable attention is devoted to studying the phase transformations of water, the hydration of cement and heat emission not only at above zero, but also at subzero temperatures. Results are provided from studies on the processes of concrete and cement hardening involving the use of various means of current conduction, in particular in an electromagnetic field, but also with the use of heating molds.

During the last 20 years new and significantly more thorough studies have been carried out on the physical and chemical processes of concrete hardening, and the range of factors under study has been expanded. In addition to determining the chemical properties of concrete and cement hardening at subzero temperatures, a great deal of attention is paid to the cryology of winter concreting, its deformation capacity during freezing, improving the technology of concretes which are subject to thermal treatment and freezing under widely varying conditions, and the influence of the porosity of aggregates on the properties of concrete subject to freezing.

In connection with this some concepts have undergone changes in this edition of the book. The new data acquired from studies carried out by modern methods and with the use of the latest equipment, as well as a comparison of them with the experience of reinforced concrete construction make it possible to explain many phenomena much more fully and thoroughly. In readying this book the author utilized the results not only from his own work, but also the data of studies by other scientists working in the area of winter concrete, and he also made use of materials from both Soviet and foreign literature sources.



The first section of the book is supplemented with the results of studies on the change in water's phase state, cement hydration, heat emission and concrete hardening at subzero temperatures, as well as the influence of early freezing on its structure, strength, gas- and water-permeability and resistance to freezing. Data are provided concerning the hardening of concrete during heat treatment involving the use of modern cements, additives and the technology of using various types of concrete. Individual chapters illuminate the role of the preliminary curing of a concrete mixture before placement and of concrete itself before heating, as well as the preliminary heating of the mixture. Data are analyzed concerning the use of saline additives in concrete hardening at subzero temperatures, as well as on the strength of concrete in the frozen state.

The second section of the book has been supplemented by recommendations and a discussion of the experience of winter concrete involving the use in construction of the thermos method, the various means of electrothermal treatment, as well as of concretes which harden in freezing weather, the insulation of precast reinforced concrete parts and structures with cast seams. Data are provided on the placement of concrete without artificial means of heating it in the structures. Considerable attention is devoted to the specific features of utilizing concrete under the severe climatic conditions of the Far North and Eastern Siberia. In a number of cases, for the sake of comparison the technology of winter concreting is compared with the experience of construction carried out at subzero temperatures in foreign countries.

Many of the materials which are of scientific and practical interest for persons involved in the construction industry could not be examined in this edition. Therefore it is the authors intention in the future to examine the work which he has accumulated over 50 years on the problem of winter concreting, along with the results of theoretical investigations and practical experience in a subsequent, more complete edition.

The author would like to thank the researchers of the laboratories for accelerated concrete hardening and physiochemical studies of the Scientific Research Institute of Concrete and Reinforced Concrete and other organizations with which he has maintained constant contact during this work for the aid which they provided him in preparing this book for press.



## Introduction

Concrete and reinforced concrete are the basic materials in modern industrial, electrical, domestic, highway, agricultural and other types of construction.

The capability of concrete to harden and to increase its strength both in the air and underwater, the possibility of using concrete and reinforced concrete to erect various structures and facilities depending on their purpose and operating conditions, and the reliability and length of their service life have long attracted the attention of builders.

In order to imagine the scales on which concrete is used in various countries and areas of the building industry, we should note that in the Soviet Union and the USA the amount of it is already calculated in hundreds of millions of cubic meters per year. Every year throughout the world, in erecting buildings and facilities of various types almost half a billion cubic meters of concrete is placed. In this case concrete is used everywhere under severely cold climatic conditions and in hot and dry areas.

We may consider that the prototype of modern concrete is the building material which was used and described by Vitruvius as early as the first century B.C. An artificial stone material was manufactured on a base of lime and hydraulically active substances such as pozzuolana and packed brick with rock fillers and was used to construct roads and sea embankments. Vitruvius says that by using the proper composition and good packing it is possible to obtain a material which "with time provides the property of firm strength even to jetties erected on the seashore". Vitruvius notes that rubblestone obtained from quarries should be used for masonry only after it is seasoned in the open air for 1-2 years. During this time the rock which is strongly saturated with moisture loses some of its water, and therefore does not break its casting when it freezes in the winter. This building experience of the ancient Romans should also be used today when we use coarse saturated stone which will be subjected to freezing in concrete. The lower the temperature below zero and the greater the degree of moisture saturation in the material, the greater is the danger that cracks will appear.

Pliny (who lived in the first century AD and died during the eruption of Vesuvius) in his encyclopedia "Natural History in 37 Books" noted that the Romans added calcinated and ground clay, ground brick or volcanic ash to lime. In ancient times and during the Middle Ages many structures (aqueducts, reservoirs, roads, etc.) were built with a mortar and concrete on the basis of this extremely simple hydraulic binder. In the south of our country this concrete is observed in the remains of buildings from the IV-VII centuries. The remains of the Uspenskiy Cathedral in Kiev indicate the use in the XI century of a mortar consisting of lime and crushed brick. In the XVII century construction in Moscow of the Sukharevskiy Tower which

was torn down in 1935, a lime mortar with a ground brick additive was also used during laying. Upon testing the solution taken from the large seams of the masonry, its strength corresponded to grade 50.

The invention of the cement which is very solid and which served subsequently as the basis for the manufacture of reinforced concrete is usually dated in 1824 when a patent was issued in England to the stone mason Aspdin. A similar elementary cement obtained by roasting a mixture of lime and clay is described in the book published in 1825 by Ye. Cheliyev in Russia. As the head of a construction command in the restoration of the Moscow buildings which suffered from fire damage during the Napoleonic War in 1812, Ye. Cheliyev developed means of producing cement and justified it scientifically.

Modern portland cement was the result of a long search by scientists in many countries and the perfection of its technology. A particularly large amount of work was done in this direction after the invention of reinforced concrete in the 1870's. Consequently, portland cement and reinforced concrete have a rich 100-150 year history. In Russia reinforced concrete was first used in building industrial, trade, port and railroad facilities. The most extensive use of reinforced concrete is noted in the capital and in the southern portion of our country since it is there that the first cement factories were built, and the metallurgical factories were able to provide structures made of steel. In addition, the fact that these cast structures were erected in regions with a short winter was important.

In connection with the beginning and the rapid development of concrete and reinforced concrete construction in all of the industrially developed countries of the world, experimental and theoretical works were organized in this area.

Some well-known Russian investigators of the pre-revolutionary period are Professor N. A. Beleyubskiy, N. A. Zhitkevich, I. G. Malyuga and A. R. Shulyachenko.

A. R. Shulyachenko is the founder of the theory and practice of the factory production of portland cement in Russia. It is well known that one of the oldest factories, the Glukhoozerskiy Factory which produced portland cement and was constructed in 1884, was founded and developed under the direct technical guidance of A. R. Shulyachenko. He directed the construction and outfitting of the second factory to produce portland cement: the Vol'skiy Factory which is still the basis of a whole group of factories which produce high quality cement. By 1903 36 factories producing 8 million barrels of cement per year were already operating in Russia. Together with N. A. Beleyubskiy and I. G. Malyuga, in 1881 Professor A. R. Shulyachenko developed the first technical conditions in Russia for cement which at that time was still being imported from abroad.

A significant contribution to the Russian science of concrete was made by Professor I. G. Malyuga who in 1895 published in the "Engineering Journal" the results of her studies on the purpose of concrete

compositions. These results were the first to give recommendations on the correct ratio of cement to water.

A great step forward which is still of considerable interest today was the book of Professor N. A. Zhitkevich entitled "Concrete and Concrete Operations" published in Petersburg in 1912. In the chapter entitled "Means of Erecting Facilities" in this book there are some recommendations on how to carry out concrete operations during freezing periods. These recommendations mainly amount to heating the materials which make up the concrete and carrying out the work in large winter shelters raised above the entire structure.

Rules for designing reinforced concrete structures were first published by N. A. Beleyubskiy in 1904. In 1908 the Ministry of Communications Routes set forth the first technical conditions for the erection of reinforced concrete facilities in Russia which govern the quality of the cement, the reinforcement, the aggregates and the concrete. As early as 1913 approximately 3.5 million cubic meters of concrete had been laid, whose manufacturer had required more than 1.5 million tons of portland cement and whose structural reinforcement had required approximately 340,000 tons of steel, i.e., 8% of the entire production of Russia. During this year a total of 1.8 million tons of portland cement were produced.

Due to the First World War and then the Civil War the economy of our country suffered great losses. The smelting of steel decreased twenty-fold by the year 1921. And the production of portland cement fell by twenty-eight times. During the period of the Civil War, on the initiative of V. I. Lenin the Soviet Government adopted a number of decisions to revive the economy, including the initiation of construction on the firstling of Soviet energy: the Volkhovskiy Hydroelectric Plant. In 1920 Lenin's plan of the State Commission for the Electrification of Russia was adopted as the basis for the future development of our country by providing electricity to the entire economy.

Even in the first years of the reviving and reconstruction of the Soviet economy, concrete and reinforced concrete were commonly used in construction. Thermal-power and hydroelectric power stations with a complex of hydrotechnical facilities were completely constructed using these materials. As a whole, many industrial buildings, refrigeration units, elevators, shore and port facilities were made of cast reinforced concrete. During this period more than 18 million cubic meters of concrete and reinforced concrete were used in the construction industry. At the Volkhovskiy Hydroelectric Plant such great specialists as Academicians G. O. Graftio and B. Ye. Vedeneyev, Professors N. N. Luknitskiy and I. I. Kandalov worked. They successfully used reinforced concrete caisson foundations in constructing a dam on fissured limestones. The methods which they successfully used in constructing reinforced concrete caissons were regarded by European specialists as being the most suitable of all.

In 1945 the "Temporary Technical Conditions and Standards for Designing and Erecting Reinforced Concrete Facilities" were developed which



regulated the compositions of concrete in addition to the design and rules for construction. Five grades of concrete were established with ultimate resistances of 8-20 MPa with a portland cement expenditure of 150-350 kg/m<sup>3</sup>. The implementation of concrete and reinforced concrete operations during winter was permitted only in winter shelters at a temperature above 5°. During the winter months builders resorted to such operations only in individual cases. The construction industry was a seasonal branch of the economy. This was accepted practice not only in the Soviet Union, but also in foreign countries. New methods of carrying out operations associated with the use of concretes and mortars under winter conditions had not been developed anywhere.

During the restoration period all of the scales and rates of construction which had been developed posed a number of complex problems concerning the proper use of building materials and structures. It was necessary to carry out theoretical and experimental studies. In connection with this, in 1927 in Moscow the State Building Institute (SBI) was founded, the successors of which were the Central Scientific Research Institute of Industrial Structures and the still-existing Scientific Research Institute of Reinforced Concrete and Concrete and the Central Research Institute of Structural Parts, as well as the Central Scientific Research Institute for Organization, Mechanization and Technical Aid in Construction and a number of other specialized scientific research institutes for the construction industry.

The works of Professor N. M. Belyayev (Leningrad) and his school were of great significance in the development of the modern technology of concrete in the USSR. In 1927 he put out a brochure which presented the method for the scientifically sound selection of a concrete's composition. In the development of concrete technology Professor I. P. Aleksandrin, whose book "Structural Monitoring of Concrete Quality" lasted through six editions also played a certain role.

Since the 30's the school of Academician K. S. Zavriyev in the Transcaucasus and Professor B. G. Skramtayev in Moscow developed new and better methods of calculating and selecting a concrete's composition. During the first Five Year Plan, a great deal of attention was devoted to the economic expenditure of portland cement which not only made concrete cheaper, but also improved its technical properties (it reduced its shrinkage and creep, and reduced heat emission in the erection of large facilities).

The V Congress of Soviets adopted the law governing the first Five Year Plan for developing the USSR's economy. In 1929 builders were given the first indications of the need to shift to the year-round conduct of building operations. A number of sections of the USSR State Plan and the Supreme Council of the National Economy recommended a comprehensive expansion of the use in construction of reinforced concrete as one of the cheapest and most reliable structural materials which ensured savings in a metal which was in very short supply. In the years 1930 and 1931 cast reinforced concrete was used to erect the Gosprom [State Industry] Building in Khar'kov and a large number of multi-story buildings, and in addition support structures were built in the

Khar'kov Tractor Factory, in factories in Moscow, Sverdlovsk, Rostov and other cities. In addition to cast concrete, 1930 saw the beginning of the use of pre-fabricated reinforced concrete beams in industrial shop buildings, for instance at the Khar'kov Turbine Factory and in the machine rooms of the Nizhnesvir'skiy and Verkhnesvir'skiy Power Plants.

However, the first major objects of the first Five Year Plan were erected in winter in winter shelters in which artificial "summer" conditions were created, but this required an extremely great expenditure of labor by the workers and the use of timber and fuel. Thus, in the winter of 1930/1931 the building of the thermal power plant in Bobrik Donskiy was constructed in winter shelters 19 m high (Figure 1), and the building of the coal-tar chemical factory in Kuznetsk was constructed in similar shelters (Figure 2).

At that time development had just begun on more economical methods of carrying out reinforced concrete operations in winter. In constructing the chemical combine in Bobrik Donskiy some of the structures were erected in winter shelters, and some of them were heated by the "thermos" method, and the massive foundations under the blast furnace and blast-heaters at the Nagnitostroy were completely cast in concrete using the "thermos" method.

Beginning with the winter of 1930/31 Mosstroy (the Moscow Construction Project) erected several residences in the normal way by heating materials, but later used the freezing method. At the time ferroconcrete operations were carried out only in large-scale winter shelters.

Beginning in 1929-30 during the winter months, large-scale reinforced concrete operations began in Leningrad to construct the industrial buildings of the "Red Putilovets" (now the Kirovskiy Factory). Frame reinforced concrete structures were erected with the material heated in steam jackets. The equipment of the large-scale winter shelters required great expenditures of work, timber and fuel, but the thermos method for medium-sized structures on the cements of that time did not ensure that the concrete would cure for a long time at above zero temperatures until it reached the required strength. Electrical heating of the concrete had not yet been developed for practical use.

The seasonal nature of the building industry caused great economic losses, and mainly delayed the completion dates and start-up dates of the completed facilities. This was one of the basic reasons for the fact that the construction industry lagged behind other leading branches of the economy with regard to technology and organization.

In connection with this the Resolution of the XVII All-Union Party Conference in 1932 issued a directive eliminating seasonality and ordering a shift to construction throughout the year with the



comprehensive use of the experience of the largest building organizations and growing cadres.

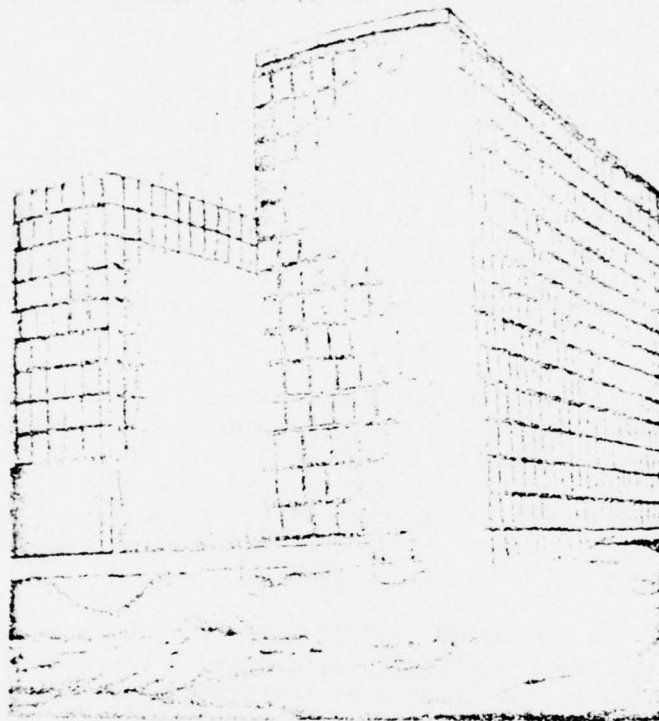


Figure 1. Plywood Sheet Winter Shelters Used in Constructing the Buildings of the Thermoelectrical Power Plant in Bobrik Donskiy in the Winter of 1930/31.

Modern industrial building is completely unthinkable without year-round employment of workers and engineering and technical cadres, complex machines and apparatus, as well as large pre-fabricated structures which are sent to the construction sites from factories and casting yards. Now when the methods of winter brick-laying and of accomplishing reinforced concrete operations have been developed and introduced, construction is carried out during the winter months almost as easily as during the summer months. While previously excavators, bricklayers, concrete workers, fitters, and carpenters stopped work and left for the country for the duration of the winter after it arrived, now they work on construction operations throughout the year. Because, for instance, the method of freezing brick work has been developed and introduced, these operations are now carried out out in freezing weather with only the mortar being heated in order to make it easier to lay. Methods have been mastered for carrying out plastering and finishing operations at subzero temperatures.



Figure 2. Winter Shelter Erected in the Winter of 1930/31 in Constructing the Coal-Tar Factory in Kuznetsk. (Under the burlap tents trenches are being dug.)

Broad-scale scientific experimental work which had been carried out in a number of areas aided in eliminating seasonality in construction.

The gradual shift to year-round construction operations can be judged from the data of the distribution of expenditures on construction operations by quarters given in Table 1.

TABLE 1. COMPLETION OF BUILDING OPERATIONS BY QUARTERS IN PERCENTAGES RELATED TO THE ANNUAL SUM

Кварталы года	1929	1935	1937	1951	1953
	Союзстрой ВСНХ	Главстройпром НКТП	Строительство всех министерств	Министерство строительства	
I	6	15,5	18,2	15	19
II	14,5	23,1	26,4	25	25
III	43	29,9	29,5	30	30
IV	36,5	31,5	25,9	30	26
Итого . .	100	100	100	100	100

Key: 1, Soyuzstroy of the Supreme Council of the National Economy; 2, the Glavstroyprom of the People's Commissariat of Heavy Industry; 3, Construction by all Ministries; 4, Ministry of construction.  
Commas indicate decimal points.

From the table [9, 33] it is evident that even on large industrial construction projects in 1929, only 6% of the annual program was completed in the first quarter. On small structures construction work was almost completely halted during these winter months. The maximum percentage of completed work during the year starts to drop by the third quarter, and by the end of the year the rate with which the work is accomplished usually begins to drop again. In the second Five Year Plan the scope of work carried out by annual quarters is distributed more uniformly. If the scope of work carried out in the third quarter of 1929 is seven times greater than in the first quarter of this year, then as

early as 1945 the amount of work carried out in the third quarter is only twice as large as that carried out in the first quarter.

The more uniform distribution of the amount of work by months and quarters of the year aided in reducing the turnover of the worker cadres. In the second Five Year Plan the reduction in the number of workers during the winter months was no more than 20% of the peak number of workers employed in June and July. In the period after the war (1951-1953, as is evident from the same table) the distribution of construction operations was stabilized throughout the year. However, despite this fact, due to the departure of workers in winter from small projects and the low level of the technical support provided to these projects, as a whole throughout the Soviet Union capital investments in the first quarter were only half of the investments carried out in the third quarter. On large projects these variations were considerably less pronounced. In the first quarter of 1953 the amount of capital investiture in the Ministry of Construction decreased by 1.6 times in comparison to the third quarter, and on the projects of the Ministry of the Petroleum Industry it decreased by 1.5 times.

When the latest achievements of science and construction technology are introduced, and especially when large blocks and pre-fabricated structures are widely used, the expenditures made on construction projects in each year are distributed more evenly throughout the quarters and months of the year. As an example Table 2 shows data concerning the intensity of concrete placement by quarters throughout the years 1952-1954 in constructing the Kamskiy water engineering system [47].

As is evident from the table, when building in fairly severe climatic conditions the quantity of concrete operations is distributed over the quarters as a function of the overall operational plan. In the first quarter of 1954 it was necessary to place more concrete than in the second and third quarters, and the operations were carried out regardless of the cold period of the year.

Modern methods of winter construction were developed as a result of continuous sampling and improvement of numerous suggestions. A great deal of creative work has been carried out for 45 years in this direction in the State Construction Scientific-Research Institute, the Central Scientific Research Institute of Industrial Structures, the Scientific Research Institute of Concrete and Reinforced Concrete, the Central Scientific Research Institute for Organization, Mechanization, and Technical Aid in Construction, the Central Scientific Research Institute of Structural Parts, the Central Scientific Research Institute of Construction, the B. Ye. Vedeneyev All-Union Scientific Research Institute of Hydraulic Engineering, the Krasnoyarsk Scientific Research Institute of the State Institute for Industrial Construction Design, the Southern Scientific Research Institute of Industrial Instruction, the Scientific Research Institute of the Main Administration for Housing and Civil Engineering Construction in Moscow, the Central Scientific Research Lab for the



Electrification of Industry and Construction, the Scientific Research Institute of Roads, the All-Union Scientific Research Institute for the Construction of Petroleum Industry Enterprises and a host of other organizations. An important role was played by the laboratories of such projects as the Magnitogorsk Construction Project, the Kram Machinery Construction Factory, the "Builder" Trust, the Tagil Construction Project, the Moscow-Volga Canal, the Volgadon Construction Project, the Dnepr Construction Project and the Kuybyshev Hydroelectric Construction Project, the Lenin Hills Construction Project and others.

In 1930 the engineer A. M. Ginzburg proposed a method of freezing concrete immediately after placement and layer-by-layer consolidation of it in the form (i.e., freezing before the cement begins to set). However, the experience of building a reinforced concrete bridge in the winter of 1931/1932 and the results of tests carried out at the State Construction Institute showed that this suggestion was faulty. Premature use of it in a number of projects led to serious defects and even accidents.

Early freezing of concrete required curing of the structures in the form until the onset of spring and then 28 days under warm conditions. This disrupted the concrete structure and its coupling to the reinforcement iron which led to an unacceptable drop in strength vis-a-vis the normal. Therefore modern Construction Standards and Regulations as well as the Specifications for Winter Operations do not allow premature freezing of concrete [35, 55, 67]. Early freezing is especially harmful in facilities operating under the effect of pressurized water and subject to repeated freezing and thawing in a water saturated state.

Instead of the freezing method, in 1931 Professor I. A. Kireyenko suggested a method for protecting concrete from freezing only for the period of setting and initial hardening, which he determined to be 36 hours; he used this method as early as 1910 [23]. As much a step forward as this method was, it still did not eliminate the basic disadvantages of premature freezing of concrete.

The experience of a number of projects as well as studies carried out at the Central Scientific Research Institute of Industrial Structures and the Central Scientific Research Institute of Construction led to the development of the scientifically proven "thermos" method, i.e., a method of placing concrete in freezing weather with enclosed heating of it for the required time determined from data of thermotechnical calculations of concrete cooling and the intensity of its hardening. In 1933-34 Professor B. G. Skramtayev and Professor V. S. Lukyanov developed methods for calculating concrete cooling in frameworks and large-scale structures [30, 72].

Many researchers and skilled workers overestimated the role of heat liberation during cement hardening and supported the wide use of a method of concreting in freezing weather without artificial heating of rather small-scale structures and without introducing chemical additives which accelerate concrete hardening and reduce its freezing point. In 1939 some builders confirmed that with a low water-cement ratio the concrete

and solution hardened in freezing weather just as under summer conditions. It was established by experimental tests in the Concrete and Binder Laboratory of the Central Scientific Research Institute of Industrial Structures that these erroneous assertions arose due to methodological errors made by researchers in studying samples in a frozen state.

TABLE 2. YEAR-ROUND PLACEMENT OF CONCRETE.

Facilities	Quantity of concrete placed by quarters, thousands of cubic meters														
	1952					1953					1954				
	I	II	III	IV		I	II	III	IV		I	II	III	IV	
Hydroelectric stations	30	46	62	48	186	42	49	66	28	186	33	24	33	39	129
Earthen dam sluice and coverings	12	11	29	21	73	30	48	50	28	156	40	15	16	14	85
Total according to the water engineering system	42	57	91	69	259	72	97	116	56	341	73	39	49	53	213

Many of the suggestions stated at the time in print and at various conferences were subjected to experimental testing and critical examination. More than 75 research topics devoted to problems of winter operations were worked out in the course of 45 years in the Central Scientific Research Institute of Industrial Structures and the Scientific Research Institute of Concrete and Reinforced Concrete alone. In doing this more than 150,000 test samples of concrete, mortar and masonry were prepared and subjected to different heating and freezing conditions.

The most efficient methods of winter construction have been now firmly established as a result of the work carried out by scientific research institutes and project laboratories, as well as from the rich experience of building.

Among the methods used in concrete and reinforced concrete construction, the following should primarily be included: the use of precast reinforced concrete parts and structures, electrothermal treatment, steam heating, the thermos, the use of ground heat, the use of chemical, and in particular antifreeze, additives, and only in individual cases the assembly of small-scale sectional and local winter shelters. All these methods are reflected in the standards and specifications as well as in the industrial manuals



which are periodically revised, with the expansion of the range of application and the utilization of results of studies and the rich experience of construction organizations [51, 66, 68].

Winter construction methods developed in the years of the First Five-Year Plans played an enormous role in the years of the Great Patriotic War, especially when it was necessary to quickly erect buildings for immediate use of the equipment of enterprises relocated in the East. Under conditions of prolonged severe freezing weather in the Urals and Siberia in winter 1941/42 and 1942/43, builders successfully carried out the assignments of the party and government by using advanced methods of winter concreting and brick-laying in freezing weather.

The construction of buildings of not only individual shops but entire factories began and ended in the winter months. Scientific workers who had been previously occupied with the research and development of specifications and manuals on winter construction worked on projects with the greatest defense value to render engineering assistance.

As a result of the experience of building during the war years, new methods were developed, such as peripheral electric heating, electrical heating of mortar poured under facilities, concreting on a frozen foundation, retardation of the setting times of non-cement plasters, acceleration of hardening of mortars by introducing various additives, steam curing in a "capillary" form, electrical heating of brickwork and rough walling. Work on establishing the optimum temperature conditions for hardening concrete was further developed. Methods of heating concrete and reinforced concrete structures of various types with heat carriers were developed and used in a number of cases. The experience accumulated made it possible for builders to restore damaged and erect new buildings and facilities in winter in the post-war period in unusually short times.

Builders and workers in the construction material industry made a great contribution to the development of methods of winter concreting in the Soviet Union in the post-war Five-Year Plans.

The introduction of quick-hardening cements and concrete with large additives of salts which enable it to be used at sub-zero temperatures, the change to industrial construction methods and the wide use of precast reinforced concrete structures associated with this considerably changed the technique of winter construction using reinforced concrete. The shift to large-scale use of precast reinforced concrete in accordance with the decision of the Central Committee of the CPSU and the Council of Ministers of the USSR of August, 1954 transformed the building site to a considerable degree into an assembly site for precast units and factory structures. In doing this the winter aspect of construction operations is only partially preserved in the in situ casting of joints of precast reinforced concrete structures. The introduction of quick-hardening concretes into production also made it possible to reduce the times of thermos curing and thermal treatment of structures at sub-zero outside air temperatures.

Broad development of the production and use of precast reinforced concrete structures and units lead to an increase in quality, acceleration of rates and an increase in the economic efficiency of construction. In doing this facility start-up times are sharply reduced due to the successful performance of operations at any time of the year and under any climatic conditions. The vigorous growth of the cement and precast reinforced concrete industry in the country promoted the development of construction scales and rates. By 1973 the output of cement had reached 109.5 million tons and that of precast reinforced concrete 102 million cubic meters. Methods of erecting buildings and structures under summer as well as winter conditions changed radically with this development of the use of precast reinforced concrete construction.

Valuable experience was accumulated in the area of winter concreting, bricklaying and facing operations in the construction of tall buildings carried out between 1949 and 1955 and of modern multistory frame-and-panel, cast in situ and frame constructions with various types of enclosing panels.

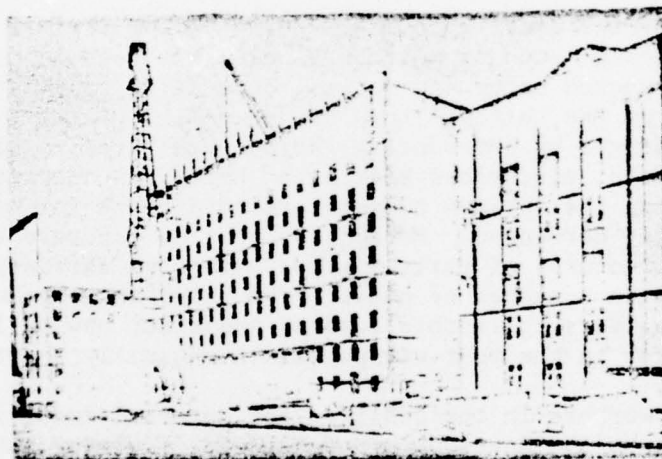


Figure 3. Assembly of Multistory Housing Structures of Precast Units in Moscow on Marshal Zhyukov Prospect.

The development of a new method of winter concreting based on using antifreeze additives is a great achievement.

Modern methods and techniques of concrete and reinforced concrete construction at sub-zero temperatures are represented in Figures 3 and 4. In these cases all the work done in freezing weather is carried out in exactly the same manner as under ordinary summer conditions. Materials comprising the concrete in the latter case can be used without heating, and the structures are not heated after placing the concrete. It is sufficient to cover the exposed surfaces of the concrete to protect them from the direct action of frost, wind and precipitation [29, 37]. The difference in the technique of performing operations under winter and summer conditions which still existed several years ago is gradually being reduced. The spacious winter shelters used previously has become a part of history.

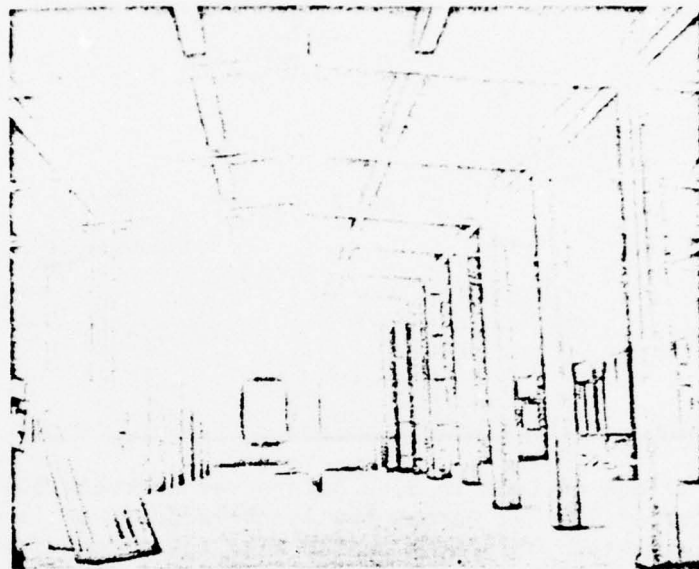


Figure 4. Reinforced Concrete Structure of an Industrial Building Built in Voronezh in the Winter of 1953/54. The addition of salts made it possible to use the materials without heating and it was not necessary to heat the concrete of the structures in freezing weather.

The method of electrically preheating the concrete mixture before placement in a form which was first suggested by A. S. Arbenyev [1] in 1962 played an important role in development of methods of winter concreting, particularly electric thermal treatment. This method, which was developed in the Novokuznetsk Department of the Ural Scientific Research Institute of Construction Machinery Design and the Scientific Research Institute of Concrete and Reinforced Concrete, is widely used in the winter constructions of various ministries and departments. In many cases electrical heating of the concrete mixture at the placement location up to a temperature of 60-80°C in conjunction with the thermos method and the introduction of chemical additives fully ensures favorable conditions for concrete strengthening necessary for dismantling structures in freezing weather. In winter 700-800 thousand cubic meters of concrete are placed annually using this method throughout the Soviet Union on the whole. A reinforced concrete bridge built during the winter months (before the advent of hot weather) by the Pechora Shaft Construction Project in the Vorkuta Region is shown in Figure 5. The concrete mixture delivered from the concrete factory was heated in bunkers before placement in the form work. The structures were heated in severe freezing weather, especially when the surface modulus was great, to ensure the necessary curing period of them before freezing.



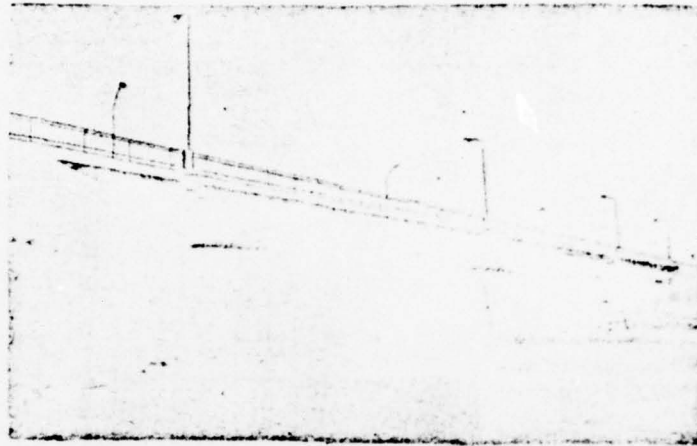


Figure 5. Bridge of Cast In Situ Reinforced Concrete Built in the Winter of 1971/72 Across the Ayach-Yachu River in Vorkut. The concrete mixture was first heated near the placement location in a heated form, with partial erection of local winter shelters during high winds.

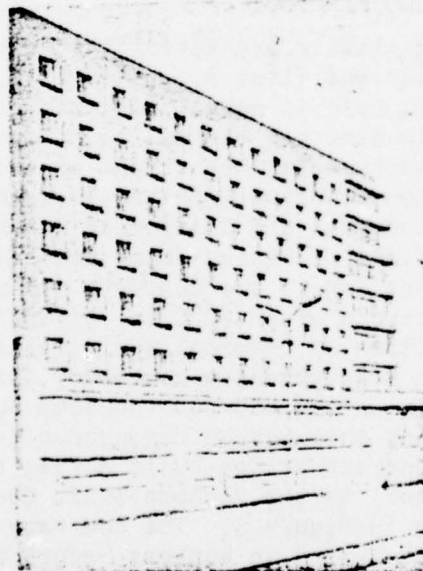


Figure 6. "Lena" Hotel Building Built in 1972/73 in Yakutsk on Permafrost Ground. Electrical heating of the concrete was used in erecting the grating on a pile arrangement and supporting structures.

Construction under the severe climatic conditions of the far north and the permafrost regions is expanding and being enriched with new experience as each year passes. The latest successes were achieved by builders in erecting structures in Vorkut, Norilsk and Yakutsk. Multistory buildings for various purposes are now erected in these areas on permafrost soils due to the change to pile construction (instead of continuous footings which were previously used). Instead of heating the concrete placed in the footings and piles embedded in permafrost soil, the author's suggestion concerning the computation of concrete strengthening at near zero temperatures is being used in a number of cases. If we consider that the temperature of permafrost soils usually varies from  $-0.5$  to  $-5^{\circ}\text{C}$ , it is enough to use a small quantity of chemical additives to harden the concrete. Figure 6 shows a general view of the eight-story hotel "Lena" built in Yakutsk. The hotel was built on a pile arrangement. Construction operations on the hotel building were conducted year-round. During the winter months the temperature of the outside air dropped to  $-50^{\circ}\text{C}$ .

The amount of investments increases with each year and each Five-Year Plan. If we consider that almost 60% of all the resources earmarked for capital construction are expended on construction assembly operations, it will become clear why so much attention is devoted to the question of eliminating seasonal influences in construction, to the introduction of advanced technology and to the development of the construction industry.

At the contemporary stage of development of technology concrete, reinforced concrete and stone designs are basic in erecting capital buildings and facilities. The great consumption of metal by other sectors of the economy and the limited possibilities of using lumber have made concrete, reinforced concrete and stone materials not only the leading materials in construction of recent years, but have firmly established them as such for the coming years. The use of concrete and reinforced concrete has a great future in many Ten-Year Plans.

At present the volume of concrete and reinforced concrete construction carried out annually is measured in tens of millions cubic meters. At present already more than 70% of all supporting structures in construction are made of reinforced concrete. Almost 60% of urban residential buildings are erected using reinforced concrete panels and concretes of various types, especially light concrete. Of all the materials used for walls, i.e., for the enclosing structural members of buildings of various purpose, approximately 50% is lightweight aggregate [Keramzit] concrete. In 1970 in the Soviet Union 96 million cubic meters of cast in situ concrete and reinforced concrete were poured, and with each year the amount placed increases. In this case 30-40% of cast in situ concrete and reinforced concrete is placed under winter conditions, i.e., at sub-zero temperatures when it is necessary to resort to special methods of carrying out the operations.

The same can be said about structures and masonry of natural and artificial stone materials. These materials and structures are also used



on a large scale in our capital construction and together with reinforced concrete are essential in building cities as well as industrial and other capital facilities. Recently it has found wide use in agricultural and road construction.

The amount of concrete work in hydrotechnical installations is especially great. For example, 180,000 cubic meters of concrete were poured at the Dnepr Construction Project, 2,957,000 cubic meters on the Moscow Canal (Moscow-Volga), 2,290,000 cubic meters at the Volga Construction Project, 2,960,000 cubic meters at the Volgodon Construction Project.

Even larger quantities of concrete and reinforced concrete are used in Volga and Siberian hydrotechnical plants. Hundreds of thousands of cubic meters of concrete have been poured at such large-scale industrial facilities as the Magnitogorsk Construction Project, the Kuznetsk Construction Project, the Cherepovets Metallurgical Construction Project, the Tagil Construction Project, the Zaporozh Construction Project, the Kammenskoye Automobile Factory, the Pechora Shaft Construction Project, the Norilsk Combine, etc.

The seasonal nature of construction tells painfully on construction itself as well as the economy on the whole. This seasonal character causes turn-over of working cadres, lost time in the operation of machinery and mechanisms, creates great difficulties in connection with fluctuations in material requirements and transport of it and delays the start-up of necessary facilities. Therefore, attention is drawn to the elimination of these seasonal effects in all countries. As early as the 1920's a special committee was created in the U.S.A. which worked a long time on exposing losses in various branches of industry. In doing this especially great attention was devoted to eliminating seasonal influences in construction since, according to the conclusions of the committee, "a slowdown of the building rate causes a reduction in activity in other branches of industry as well".

Continuity of production in all branches, including construction, is necessary under the conditions of a planned socialist system in the economy for maximum development of the productive forces of the nation. Methods of winter construction using concrete, reinforced concrete and stone materials which have been developed in the Soviet Union have promoted the conversion of construction from an unsystematic and seasonal sector of the economy into an industry which works year-round with permanent cadres of qualified workers.

Besides the enormous economic effect of eliminating seasonal influences in construction, each construction organization economizes in real terms as the result of fulfilling a set construction plan with the fewest number of permanent workers, better use of machinery and equipment, reduction in construction times as well as by reducing unprofitable expenditures. The economy on the whole and the individual enterprises received large benefits in doing this due to the more rapid start-up of buildings and facilities. The activation of new large-scale industrial enterprises, for example in the years of the First Five-Year Plans, was characterized by the following data: for 1928-1932, 1500 units, for 1933-1937, 4500 units.

The use of such production methods as the thermos, electric heating and steam curing, instead of spacious winter shelters, saves hundreds of millions of rubles throughout the Soviet Union on the whole. An even greater effect is achieved with the broad utilization of precast reinforced concrete structures and large-scale units in winter, and also by using preheated concrete mixtures and concretes which harden in cold weather.

The increase in the cost of winter operations can be considerably reduced by the correct choice of operating methods. The smallest rise in cost of operations is obtained in assembling factory-made reinforced concrete designs, in erecting large-scale structures (hydrotechnical facilities, furnace and heavy equipment foundations, and so forth) as well as in placing concrete which hardens at sub-zero temperatures. When using precast reinforced concrete designs in winter the rise in the cost of assembling them is comparatively small. As experience shows, it is advantageous to use the thermos method in erecting large-scale cast in situ concrete and reinforced concrete above-ground and below-ground facilities with a surface modulus of less than 5 in winter. It is advantageous to erect structures with a surface modulus of more than 5, as a rule, using various methods of electrothermal treatment. The latter is most flexible in continuous production and is not associated with extensive factory equipment.

Research is being carried out in many foreign countries on the problems of theory and practice of winter concreting. In Europe in such countries as England, Belgium, Denmark, the GDR, the FRG, Norway, Poland, France, Finland, Czechoslovakia, Sweden, in America, Canada, the U.S.A., in Asia, in Mongolia, China and Japan, where winter construction is of great economic significance. Due to different climatic conditions questions of theory and practice of winter concreting are of less interest for builders in other countries or do not interest them at all. The amount of work is being sharply reduced in a number of countries due to the short winter period of 1-3 months. In these nations, such as England, France, Switzerland (except for mountainous regions), simpler methods of placing concrete are used at temperatures just below zero.

Steam and hot air, less frequently electrical energy, are used to heat water and aggregates as well as to warm the concrete in construction. In France it is used, as a rule, at night when electrical energy is 5 times cheaper than in the day. In the prewar period only isolated cases of the use of electrical heat in the winter projects of certain countries was noted. In the postwar period this method became quite widely used in projects in the northern part of Japan, in France, the U.S.A., Finland, Belgium and even in such countries as Italy, Portugal, Spain.

The thermos method based on warming the structures to retain heat introduced into the concrete by warming the materials as well as that liberated during cement hydration is used quite widely. The research and methods of calculating concrete cooling in freezing weather which were worked out by Ya. Gronholm in Sweden [83] on this problem are well-known.

Quick-hardening cements are used and buildings and facilities erected of precast structures to simplify and reduce the cost of winter construction. In this regard great advances are being made in England, France, the GDR, the FRG and Czechoslovakia. Industrial and civil buildings, heat and electric power plants, bridges, hangars, and so forth are being constructed of precast reinforced concrete designs. The use of this method meets to a very great extent the requirements of industrialization of construction and ensures the high quality of facilities erected at sub-zero temperatures.

Admixtures, concrete hardening accelerators, are used primarily together with workability agents. The addition of calcium chloride in amounts of 2-3% by weight of cement together with air entraining and workability admixtures as well as the use of quick hardening cements and concrete mixtures with a low water-cement ratio is an independent method of winter concreting in countries with a moderate climate.

A large amount of literature is published overseas on problems of winter construction. Official industrial manuals and handbooks for construction have been developed along with the publication of individual works and articles in the U.S.A., GDR, FRG, Denmark, France, Finland, Sweden on these problems.

As is apparent from the recommendations for winter concreting published in the journal of the American Concrete Institute and from the report of a Belgian commission which studied the experience of winter concreting in Denmark and Sweden, foreign methods of concreting in freezing weather differ little from those existing in the USSR. Our methods of concreting are distinguished by their diversity and the use of more complete, although more complex (as, for example, electrical heating and warming and others) operating methods. In the U.S.A., just as in other European nations such as Belgium, GRD, the FRG, Denmark, Sweden, materials are preheated with live steam, but in a case of smaller operations, by fire, sometimes in special drums and bunkers. In European and Scandinavian countries, coarse aggregates are frequently not preheated. Concrete poured into a structure is most often cured with thermos cooling which uses mineral as well as the simplest thermal insulation organic materials (thatch board, straw, cardboard) in doing this. Light canvas or plywood winter shelters are used at lower outside air temperatures and wherever required by the conditions of the production process. The winter shelters are heated by steam and warm air up to a temperature of 20°C, and in some cases up to 30-40°C. In Finland, winter shelters and spaces inside multistory buildings cast in situ with an outside layer of gas concrete blocks are heated with wood and coke ovens and with improved oil fueled braziers.

The First International Symposium on Winter Concreting was held in Copenhagen in February 1956. This symposium was organized by the International Association of Scientific-Research Laboratories for Studying and Testing Building Materials and Structural Elements (RILEM).

Delegations from 18 nations participated in the symposium: England, Australia, Belgium, Holland, the GDR, the FRG, Denmark, Canada, China,



the USSR, the U.S.A., Poland, Norway, Czechoslovakia, Sweden, Switzerland, France and Finland. Representatives from the Scandinavian countries participated most actively. The president of the Organizing Committee was M. Plus (Denmark) who then headed the Winter Concreting Committee. Such outstanding scientists as Professors G. Westlund, Ya. Gronholm, A. Nikenem, P. Nerenst, G. Rush, A. Collins, I. Lis, T. Powers et al., took an active part in preparing and conducting the symposium.

The Soviet Delegation gave five reports concerning:

Methods of winter concreting used in the Soviet Union (Professor S. A. Mironov); a principle of unified classification of concretes according to precalculated resistance to freezing (Doctor of the Technical Sciences, S. V. Shestoporov); the effect of air entraining admixtures on the increase in concrete resistance to freezing (Professor V. B. Stolnikov); concretes which harden in freezing weather (Candidate of Technical Sciences, V. N. Sizov); winter concreting using the method of peripheral electrical heating in building the Gorkovsk hydroelectric station (Engineer K. V. Alekseyev).

Professor E. Swenson (Canada) in his report "Climatic Conditions and Their Effect on Winter Concreting" imparted interesting data on winter concreting in Canada. The report emphasized the role of the wind as the second factor after air temperature which causes cooling of the concrete, and it was noted that construction supervisors should always have an exact weather forecast, and not rely on average statistical temperatures.

Professor Ya. Gronholm (Sweden) discussed the principal factors which ensure the required quality of concrete, loading of structures, as well as timely removal of form-work from them. He devoted a great deal of attention to the correct determination of concrete strength and the prevention of deformations when removing the form-work from the structures. He noted that to do this it is necessary to determine the degree of drop in the elastic modulus of concrete when freezing at a young age.

Engineers D. Buitink and D. Trouw reported on the organization of winter operations in Holland where every attempt is made to conduct them - with the simplest and least expensive methods. In essence, quick-hardening concretes are produced by heating the materials, using special cements with a low water-cement ratio, adding calcium chloride and so forth, covering poured concrete with thermal insulation materials. At temperatures from -5 to -10°C concrete is heated with steam in light winter shelters as a last resort. In cases in which the outside air temperature falls below -10°C, work generally stops.

H. Grener (Norway) noted that in Norway temperatures are below zero 6-7 months of the year. Therefore winter concrete is an important economic problem for Norway. Nevertheless the simplest methods of protecting concrete from freezing are generally used in Norway (heating the water in the aggregates, heating the form-work and reinforcement with steam).

A. Nikenem, B. Kelopuu and A. Yunttila reported on winter concreting in Finland. It is apparent from the data of the study of A. Nikenem of 25 projects that materials are generally heated with steam in Finland, just as in Norway, Sweden and other countries. Freshly poured concrete is covered with straw mats, cardboard, sheets of wood shavings, mineral wool, canvas and burlap.

In Denmark and Sweden more simple furnaces of a type of improved oil fueled brazier are used to heat winter shelters.

E. Backhaus (FRG) reported on an operating method used in November-December, 1954 in building a reinforced concrete television tower in Stuttgart. With the advent of freezing weather work on erecting the tower at the mark level from 65 to 135.7 meters was carried out in a mobile canvas winter shelter with air heating. Metal form-work was heated with a 3 cm slag layer. The air temperature within the winter shelter was maintained at a level of 10-15°C. As work on the tower proceeded the winter shelter was raised 1.57 meters daily. Before placement the concrete mixture was heated with steam to 20°C. Type 400 concrete was used with consumption of portland cement at 320 kg/m<sup>3</sup>. This same operating method was used in Merseburg where an 80 meter smokestack was constructed in winter.

The reports of Yatsuo Ichiki and Katsuo Kharimatsu were sent from Japan. It was clear from the reports that the Soviet practice of electrical heating of reinforced concrete structures was studied and used in Northern Japan beginning in 1946 [83].

Professor T. Powers (U.S.A.) reported on the use of air entraining additives to increase concrete resistance to freezing and on the mechanism of concrete breakdown during freezing. This speaker presented in detail a theory of the hydraulic pressure which arises in freezing concrete. He considered the organizational structure of cells of entrained air more important than the quantity of it.

As became clear from the reports of the delegates, the addition of air entraining agents to concretes is widely used in many countries in building roads, airports and hydroelectric stations. Experimental studies and observations of test objectives confirmed that air entraining additives raised the degree of concrete resistance to freezing and increase the life-time of concrete and reinforced concrete structures.

Professor A. Collins (England) presented a paper on concrete resistance to freezing in which he examined new mechanism of freezing and concrete breakdown when water changes from liquid to solid state.

Professor I. Lis (Norway) reported on the determination of the dependency of the strength of concrete of like composition at temperatures from 4.5 to 46°C.

The works of many researchers were devoted to explaining this dependency, which is important for practical purposes. Professor G. Westlund (Sweden),

P. Nerenst and E. Restrup (Denmark) reported on this same topic. The speakers from Sweden noted that in the southern part of their country where more construction takes place the temperature passes through  $0^{\circ}$  sixty times a year. The maximum common temperature gradient does not exceed  $15^{\circ}$  in this regard. Therefore, in testing for resistance to freezing they found it necessary to freeze concrete samples at a temperature of  $-10^{\circ}\text{C}$ . A temperature of  $-48^{\circ}\text{C}$ , which can be found in the northernmost areas of Sweden, is recommended for tests on unit freezing.

Professor A. Wellmi (Switzerland) presented an interesting report on producing high quality concrete under winter conditions. In discussing the possibility of repeated freezing he believes that by this time concrete should have a strength of at least 15 MPa, and the saturation factor should drop to 0.9.

Professor Yu. Gzhimek (Poland) reported on the results of his studies and on the production of quick hardening portland cement on the basis of producing fine crystalline alite. The amount of the alite crystals obtained by metastable crystallization of silicates is 15  $\mu$  on the average.

A special committee was created of representatives from interested countries after the First International RILEM Symposium on Winter Concreting in 1957. The Scandinavian countries (Denmark, Sweden, Finland), Holland, the USSR, the U.S.A., Poland, France, the FRG participated in a most representative and active manner in making up the Committee and sub-Committees.

International recommendations for winter concreting, weather forecasting recommendations, and construction recommendations were developed and published in a number of countries, including in the USSR, by the RILEM Committee on Winter Concreting. Reports on problems of winter concreting and the results of studies carried out in different countries were heard at meetings of the Committee and sub-Committees. Requirements for cements for winter concretes along with a classification of them according to heat release were developed by the Committee. In doing this the recommendations of the authors with regard to mineralogy, the fineness of cement grinding and additives to it were reflected in this.

As the result of the activity of the Committee a systematic exchange of literature and information on the results of research was established; this makes it possible to avoid superfluous research.

As the result of the exchange of experience, Committee members in different nations intensified research through their representatives on electrical heating of concrete, methods of caulking prefabricated reinforced concrete structural elements in freezing weather, introduction of chemical admixtures for winter concrete and the effect of freezing of concrete with various strengths on its properties.

Almost 20 years have passed since the First International Symposium on Winter Concreting in Denmark in 1956. The urgency of this problem has grown even more during this period. Further studies have been conducted



on studying concrete hardening processes using modern methods and measuring technique. Experience in erecting multistory buildings and unique facilities at sub-zero temperatures has been accumulated in all interested nations.

The Second International Symposium on Winter Concreting to be held in 1975 in the Soviet Union will make it possible to exchange information on the most important problems and trends in future research in the area of theory and methods of winter concreting. Methods of using available results to develop new and improve existing methods of concreting cast in situ facilities, assembling precast parts and erecting structures of prefabricated cast in situ reinforced concrete at sub-zero temperatures will be determined as the result of the knowledge of the most important achievements of science in this field.

This will be the second international forum in the Soviet Union on concrete technology and concreting methods. The first, which took place in 1964, was devoted to problems of accelerating concrete hardening in the manufacture of precast reinforced concrete. Problems of concrete technology and concreting methods in erecting cast in situ structures will be discussed at the next symposium.

PART ONE  
PRINCIPLES OF THE THEORY OF  
WINTER CONCRETING AND COLD WEATHER CONCRETE SCIENCE

CHAPTER 1  
PHASE TRANSFORMATIONS OF WATER AT DIFFERENT TEMPERATURES

Concrete, which is an artificial stone material, consists of a mixture of gravel or crushed stone and sand bound together by cement stone. The active component of concrete is the cement stone which plays an important role in the formation of its structure and strength as well as its resistance to freezing and water impermeability.

The following principal factors affect the hardening process in the physical-mechanical properties of cement stone: quality, including the mineralogical content of the cement used; water cement ratio, i.e., C/W (frequently the inverse, W/C, is used); introduced admixtures; placement density (formation of the structure when manufacturing parts and structural elements); hygrothermal curing conditions.

A favorable temperature, continuous presence of the appropriate moisture medium and time are necessary for the setting and hardening processes to take place; in individual cases special hardening conditions necessary to achieve a given strength in short periods of time must be created.

In modern concrete technology the setting and hardening times of cements are examined in conjunction with their mineralogical content, grinding fineness, the temperature factor and introducible admixtures. This enables us to more thoroughly understand the physical-chemical nature of the phenomena which occur in hardening mortars and concretes.

Many studies which have been confirmed by construction practice have made it possible to establish functions and accumulate data which make it possible to control the setting and hardening processes of mortars and concretes. If all this is of great value for concreting under summer conditions, in winter concreting the knowledge of the theory of cement hydration and concrete hardening is basic and a guarantee of the success of operations being carried out. Thus, before turning to an examination of winter concreting methods, we must discuss questions of theory and technology, the physics and physical chemistry of cements and concretes.

Since water is an invariable part of the active component of concrete, i.e., cement stone, let us first examine those changes which may occur with it at different temperatures. With regard to winter concreting the phase transformations of water during the freezing of cement stone and concrete are of special interest.

## Basic Properties and Classification of Water Bonds.

In nature water is found in three aggregate states: solid, liquid and gas. At normal atmospheric pressure water has a boiling point of  $100^{\circ}\text{C}$ , ice a melting point of  $0^{\circ}\text{C}$ . The latent heat of melting of ice is 336.6 joules at  $0^{\circ}\text{C}$ . Consequently, this amount of heat is liberated when freezing 1 kg of water, and absorbed in thawing ice. The maximum density of water at  $4^{\circ}\text{C}$  is assumed to be 1. Water is hygroscopic, i.e., adsorbed on the surface of a solid or liquid body, and easily driven off upon heating. Crystallized water in the form of  $\text{H}_2\text{O}$  molecules makes up crystalline hydrates. For example, in the hydration of cement clinker minerals one or several molecules of crystallized water are needed for one molecule of silicate oxides. The transition of water from one phase into another occurs intermittently with a change in its internal structure and all the physical properties and characteristics associated with it. All phase transitions of water (crystallization, melting, condensation, boiling and evaporation) are associated with liberation or absorption of heat. These properties of water, as a component part of concrete, must be known and used in manufacturing concrete when curing it under different temperature conditions and when maintaining structures. This is of special interest in winter concreting when special measures must be taken to create favorable conditions for concrete hardening.

The properties of concrete (hardness, strength, stability in various media) depend to a great extent on the phase state of the water contained in the concrete. In calculating concrete cooling in freezing weather, the heat of melting and crystallization of ice must be considered in the heat balance of the structure.

Different researchers classify water contained in a hardening cement paste differently.

T. Powers [49, 84] divides water in a solidified paste into that chemically bound; that physically adsorbed on the surface of the gel; that beyond the effective radius of surface forces. However, he believes that it is difficult to ascertain what quantity of water is found in what state. With chemical analyses it is impossible to exactly separate one type of the hydration products from another.

A. V. Lykov divides water in cement stone, depending on the degree of bonding energy, into physical mechanically, physical chemically and chemically bound.

Physical mechanically bound water is the free water in the cells of the crystallized structure of the gel and the water in the micro- and macrocapillaries of the cement stone. This water is retained mechanically and preserves its ordinary properties. It is usually called capillary or hygroscopic water. It is driven off by heating cement stone to a temperature of  $105^{\circ}\text{C}$ . The amount of mechanically bound water depends on the moisture and temperature of the medium. Physical mechanically bound water in the microcapillaries of the cement stone affects its strength and



deformation. The water of a monomolecular layer is bound by adsorption and its properties differ from that loosely bound.

Physical chemically bound water is found in hydrate envelopes. It appears as the result of the dissolving and hydration of minerals of the cement clinker, the particles of which adsorb the moisture. This state of water is bound by a molecular forcefield. Water in adsorbed layers changes its properties. At different temperatures, especially when cement stone and concrete freezes, it may change its phase state in a somewhat different manner than water which is physical mechanically bound. In contrast to chemically bound water, upon heating it is freely driven off in a gradual manner. Solidified cement stone contains approximately as much of it as it does chemically bound water. It may be removed from the crystalline lattice without destroying the crystals and is then reabsorbed in the moisture medium.

In freshly poured concrete the volume of added water may be conditionally considered to be equal to the volume of the pores and capillaries contained in a mixture of a different type. Besides the water contained in the capillaries and in the partially arising new formations, some of the water is separated on the surface of the structures when the concrete mixture is consolidated and it is distributed in the macropores and macrochannels of sedimentation origin. The latter is produced as the result of water rising in the process of immersing the solid components.

The dimensions of the pores, channels and capillaries containing water depend to a considerable degree on the thickness of the cement paste (W/C), the total water content in the concrete and on the degree of consolidation, i.e., on the proximity of the contacts between solid components. The channels of sedimentation origin and macrocapillaries are measured in microns and even in millimeters. Microcapillaries have a variable cross-section and are measured in tenths of microns, and the pores of the gel in angstroms.

With the passage of time the volume of the capillary pores decreases, but that of the gel and contraction pores increases. The structure of the cement stone and concrete always changes in favor of an increase of its density during the cement hydration process.

During freezing the water being frozen does not immediately change to a solid, but partially remains liquid in the form of thin films on the inner surfaces of the capillaries and in the gels even at very low sub-zero temperatures.

As the temperature drops, the amount of water in the liquid phase decreases and at a temperature below  $-10^{\circ}\text{C}$  very little of it remains. In freshly poured concrete at a temperature below  $-10^{\circ}\text{C}$  almost all the water changes to a solid state -- ice. This situation is in good agreement with the results obtained in studying hydration and heat liberation of cements as well as the strengthening of cement stone and concrete at sub-zero temperatures.

TABLE 1.1. ICE CONTENT IN HEAVY CONCRETE FROZEN AT VARIOUS AGES

Temperature °C	Ice Content of Concrete, %				
	Frozen immediately after placement	Frozen at Strength, % of R28			
		15	50	70	100
-3	91	43	20	14	10
-5	92	58	27	22	18
-10	92	66	42	38	33
-15	93	73	58	44	41
-20	94	74	63	49	43
-30	96	78	65	54	49
-45	97	87	68	57	52

According to the data of Professor T. Powers (determined using the dilatometric method), when  $t = -0.5^{\circ}\text{C}$ , 21% ice is formed in cement paste, when  $t = -4^{\circ}\text{C}$ , 60% is already frozen, and at  $-10^{\circ}\text{C}$  the amount of ice increases to 75%. A considerable portion of the water in liquid phase is preserved down to  $-40^{\circ}\text{C}$  and even to  $-65^{\circ}\text{C}$  when it freezes in the gels and contraction pores. In the laboratory for concrete hardening acceleration methods of the Scientific Research Institute of Concretes and Reinforced Concretes, E. Kh. Bulgakov, O. S. Ivanova and L. A. Belova [3, 8, 19], when preparing their candidate dissertations, conducted detailed studies of ice content (percent ratio of the quantity of ice to the weight of the chemically unbound water) in cement pastes, mortars and concretes using the calorimetric method.

In her studies O. S. Ivanova froze test samples of concrete when they reached 15, 30, 70 and 100% of 28-day normal hardening strength in the temperature range of from  $-1$  to  $-45^{\circ}\text{C}$ .

Data concerning the reduction in the amount of ice as the concrete age increased in dense aggregates are shown in Table 1.1. Crushed granite stone was used as the coarse aggregate. Grade 400 portland cement was used as the cement. The ice content was studied in the samples immediately after pouring and then beginning at age one day, i.e., when the structure had been formed and intensive hydration of the cement had begun.

As can be seen from the data of Table 1.1, the time of preliminary curing of the concrete before freezing, i.e., the degree of hydration of the cement in it, greatly affects the ice formation processes.

In samples of concrete frozen immediately after pouring, when it still contains very little gel and almost all the water is found in the pores of the intergrain space or in capillaries pores between the gel particles, i.e., in macropores in a free state, and only an insignificant portion of it is strongly retained by adsorption forces, most of the water (91%) has already become ice at a temperature of  $-3^{\circ}\text{C}$ .

An increase in the degree of hydration of cement after 24 hours of hardening of concrete under normal conditions causes a change in its porosity. Macropores become micropores; some of the capillary pores are replaced by contraction and gel pores in which water becomes ice even at

lower sub-zero temperatures. The specific surface of the cement increases. All this leads to a reduction in the quantity of free water which can be frozen, in conjunction with which the ice content of the concrete frozen within 24 hours after manufacture decreases considerably.

In all these works the temperature interval from 0 to  $-2^{\circ}\text{C}$  is specially emphasized. As studies have shown, at these temperatures water may be in an unfrozen supercooled state for a prolonged period of time, and the amount of ice formed at  $-1^{\circ}\text{C}$  did not exceed 20% in the tests which were conducted. This may explain the hardening of concrete at high sub-zero temperatures and the considerable strengthening of it which sometimes reaches 70% of  $R_{28}$ .

The presence of water in the liquid phase can promote cement hydration, but at the same time it may cause the concrete to break down when it becomes ice.

It is apparent from data obtained using an isothermal calorimeter that most of the ice in the concrete is formed when the temperature drops to  $-5$  to  $-10^{\circ}\text{C}$ . Intensified formation takes place in this temperature range due to a freezing of mechanically bound water contained in macropores with a radius of more than  $0.1\ \mu$ .

When the temperature drops further from  $-10$  to  $-40^{\circ}\text{C}$ , the amount of frozen water increases less the younger the concrete before freezing. Loosely bound water and water in fine capillaries with a diameter of less than  $0.1\ \mu$  freeze in this temperature range.

An experiment similar to one previously conducted [18] was carried out with consideration of the certain difference in the cooling rate and in the strengthening of concretes composed of fine porous aggregates compared to heavy concretes at the same sub-zero temperatures. New studies were conducted on lightweight aggregate concrete of a 1:2:2.1 composition manufactured from type 400 portland cement from the Belgorod Factory, coarse river sand and keramzit gravel from the Lianozov Factory. At age 28 days the strength of the lightweight aggregate concrete was 12.5 MPa.

The phase state of the water was determined on the same isothermic calorimeter, a model from the Geocryology Institute, according to a procedure developed earlier.

The ice content of the lightweight aggregate concrete was determined at temperatures of  $-1$ ,  $-3$ ,  $-5$ ,  $-10$ ,  $-15$ ,  $-25$ , and  $-40^{\circ}\text{C}$ . Prematuring of the lightweight aggregate cement at the instant of freezing was 0; 16; 30; 50; 65 and 100% of  $R_{28}$ , i.e., almost the same as in the study conducted previously with heavy concrete.

After calorimetric measurement the samples were treated with alcohol and dried to a constant weight at  $105^{\circ}\text{C}$ . The mass of the dry concrete



sample was within 33-40 g, the mass of the water in the sample varied from 2 to 6 grams depending on the age of the concrete at the moment of freezing. Samples of lightweight aggregate concrete frozen immediately after production were placed directly in weighing bottles. Samples of strong concrete were prepared by breaking off pieces with a mass 30-40 grams from the middle of cubes  $10 \times 10 \times 10$  cm which had been hardened to a set strength in a normal condition chamber. The quantity of ice in the sample was determined with allowance for the change in the thermal capacity of the ice in the absolutely dry concrete skeleton depending on temperature.

The thermal capacity of the ice is calculated according to the formula recommended by B. P. Weinberg, according to which  $C_I = 0.5057 + 0.001863 \theta$ , where  $C_I$  is the thermal capacity device at the calculated temperature;  $\theta$  is the calculated temperature, degrees C.

The heat capacity of the absolutely dry concrete skeleton was determined experimentally with a calorimeter at  $-7$  and  $-40^\circ\text{C}$ .

From experimental results at  $-7^\circ\text{C}$   $C_{\text{con}} = 0.733$  and at  $-40^\circ\text{C}$   $C_{\text{con}} = 0.687 \text{ j}/(\text{g}\cdot^\circ\text{C})$ .

According to the data of the Scientific Research Institute for the Organization of Industrial Construction, the thermal capacity of the concrete skeleton changes to  $0.0016 \text{ j}/(\text{g}\cdot^\circ\text{C})$ . Therefore the following thermal capacity of absolutely dry lightweight aggregate concrete depending on temperature was assumed in the calculations of ice content:

Temperature, $^\circ\text{C}$	-1	-3	-5	-7	-10	-25	-40
Thermal capacity of absolutely dry lightweight aggregate concrete, $\text{j}/(\text{g}\cdot^\circ\text{C})$	0.741	0.737	0.737	0.733	0.729	0.703	0.687

The data for determining the ice content of lightweight aggregate concrete given in Figure 1.1 show that the formation of ice in it is similar to the formation of ice in heavy concrete [19].

It follows from analysis of the results obtained that phase transformations of water in lightweight aggregate concrete, just as in heavy concrete, depend on the degree of its maturity at the instant of freezing. The intensity of freezing in lightweight aggregate concrete frozen immediately after manufacture is considerably higher than the intensity of a phase transition of water in mature lightweight aggregate concrete, since at the same temperatures a considerably smaller amount of water becomes ice in the older concrete. Thus, at a temperature of  $-1^\circ\text{C}$ , 49% of the chemically bound water became ice in the lightweight aggregate concrete frozen immediately after manufacture, and approximately 20% of

the water became ice in the concrete maintained under normal conditions for 2 days and frozen at a strength of 30% of  $R_{28}$ . At  $-10^{\circ}\text{C}$  90 and 57% of the water respectively became ice and at  $-25^{\circ}\text{C}$  90 and 68%.

Ice content in samples of lightweight aggregate concrete increases as the temperature drops. The most intensive formation of ice occurs at temperatures down to  $-10^{\circ}\text{C}$ , while for concretes of varying age the ranges of "significant" and "insignificant" phase changes of water lie within different temperature ranges.

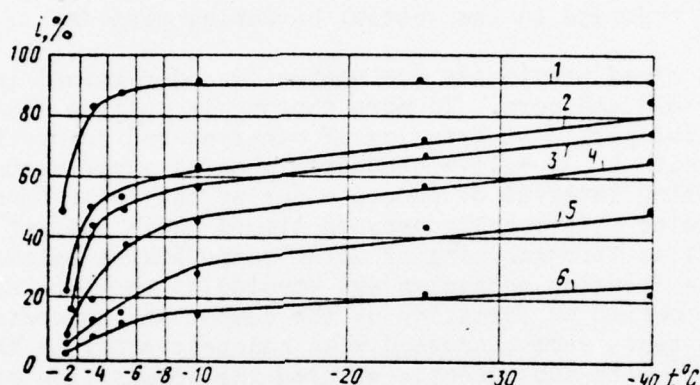


Figure 1.1. Change in the Ice Content of Lightweight Aggregate Concrete Frozen With a Varied Strength. 1, Immediately after manufacture; 2, At a strength of 16% of  $R_{28}$ ; 3, The same at 30% of  $R_{28}$ ; 4, At 50% of  $R_{28}$ ; 5, At 65% of  $R_{28}$ ; 6, At 100% of  $R_{28}$ .

For concrete immediately after manufacture the most significant phase transformations of water occur at temperatures  $-1...-2^{\circ}\text{C}$ ; thus approximately 49% of the water becomes ice at a temperature of  $-1^{\circ}\text{C}$ , and 72% at  $-2^{\circ}\text{C}$ . In concrete whose strength has reached 30% of  $R_{28}$ , the most significant phase transformations of water occur at temperatures down to  $-5^{\circ}\text{C}$ , when 68% of all the water frozen in concrete of the same age at  $-40^{\circ}\text{C}$  becomes ice.

Thus, as the "age" of the lightweight aggregate concrete increases, the range of "significant" phase transformations of water recedes from  $0^{\circ}\text{C}$  and shifts into the range of lower sub-zero temperatures.

A similar picture was observed when freezing concrete made of a dense limestone aggregate. This was due to the constant physical and chemical changes taking place in the concrete.

Concrete is a material whose structure and properties change with time. This process is especially intensive in the initial hardening period; this is indicated by the increase in strength and change in the nature of the porosity of the material. Thus, in concrete of composition 1:3.3:4.5 with  $W/C = 0.72$  the overall porosity determined

theoretically-experimentally immediately after manufacture was 18%. In day-old concrete it dropped to 17.2%, and in three-day-old concrete it was already 16.28%. The change in the very nature of the porosity during this period of time is very important. In three-day-old concrete the capillary porosity was 13.75%, contraction of porosity 0.76% and gel 1.7%. Taking into consideration that the contraction and gel porosities in the 28-day-old concrete under study were 1.28 and 2.85% respectively, we can say that in the first three days of hardening the capillary porosity drops, but the contraction and gel porosities increase by more than 50%. This confirms the considerable change in the nature of the structure of the concrete in the initial hardening periods.

In the data cited previously ice content was determined in freezing concrete one day old and more. To more thoroughly analyze what occurs in the very initial period of freezing of manufactured concrete, this author together with L. A. Belova conducted special experiments to examine the freezing interval of concrete during the first days. In doing this a regular relationship between liquid phase content and cement hydration as well as strengthening of it at temperatures below 0°C was established. The freezing mechanism was studied at the earliest stage, i.e., during the period of formation of the cement and concrete structure. At the same time tests were conducted with concrete after it attained the critical strength which subsequently ensured the acquisition of the required physical-mechanical properties. In this case samples were tested at age 72 hours.

Studies to determine the quantity of ice formed in cement paste, mortar and concrete of crushed limestone and agloporite frozen immediately and 3, 6, 9, 12, 24 and 72 hours after manufacture were also conducted using a calorimeter on the same model of the Institute of Geocryology at temperatures from -1 to -38°C. Data concerning the change in ice content of cement paste, mortar and concrete produced from Belgorod portland cement are given in Figure 1.2. The concrete was produced from crushed limestone, concrete content 1:2:3.7 at W/C = 0.58. At W/C = 0.45 the composition of the mortar was 1:3. At W/C = 0.5 grade 200 agloporite concrete was used.

As can be seen from the drawing, as the temperature dropped the amount of ice in all the components increased. In this case in concrete frozen during the first hours, most of the water becomes ice (unevenness is noted) at a temperature below -2°C, and in concrete frozen after 24 hours of normal hardening at a temperature of -5°C.

Thus, at 5 = -3°C in concrete exposed to freezing weather at age 0, 3, 6, 9 hours, 89-86% of the water freezes, and in samples hardened 12 and 24 hours before freezing 80 and 57% respectively. Most of the ice is formed when the temperature drops to -5 to -10°C, when the ice content is 74 and 78% in concrete hardened 24 and 12 hours under normal conditions, and 94% in concrete frozen immediately after manufacture.



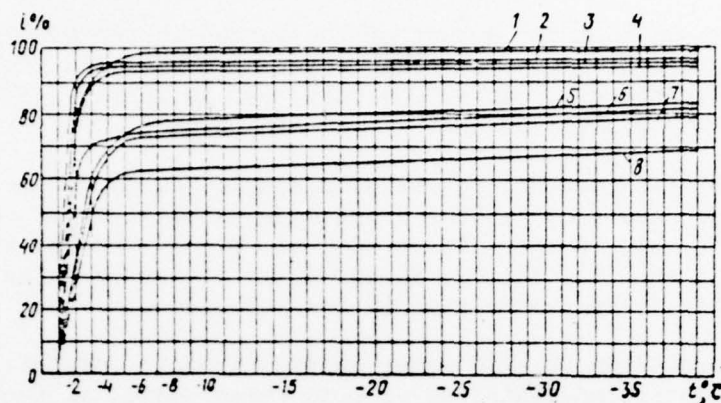


Figure 1.2. Change in the Ice Content of Cement Paste, Mortar and Concrete Frozen at Different Times. 1, 2, 3, 4, Cement paste, algoporite concrete, mortar, limestone concrete respectively frozen immediately after manufacture; 5, 6, 7, 8, Crushed limestone concrete, algoporite concrete, mortar, cement paste respectively frozen 24 hours after manufacture.

These data are in good agreement with results of dilatometric studies made by T. Powers and T. Brownyard [84], A. N. Savitskiy and D. Litvan [81] who note that intensive ice formation takes place in this temperature range due to the freezing of physically bound water in capillaries with a radius of more than  $0.1 \mu$ . When the temperature drops further from  $-10$  to  $-40^\circ\text{C}$ , the amount of frozen water increases insignificantly due to the freezing of water in finer capillaries with a diameter of less than  $0.1 \mu$ . The hardening time of the concrete before the beginning of freezing, or in other words, the degree of hydration of the cement in the water cement ratio, exerts a great effect on ice content [32]. In hardened cement a considerable amount of the unfrozen water is found in the calcium hydrosilicate gels. in the  $-40$  to  $-50^\circ\text{C}$  temperature range some increase in ice content is noted due to the freezing of water in contraction pores with a diameter of approximately  $0.05 \mu$  and loosely bound water in foreign capillaries. In pores with a radius of less than  $50 \text{ \AA}$  water freezes at temperatures below  $-60^\circ\text{C}$ . It is strongly bound in the crystalline lattice of the gel by adsorption forces, in contrast to that portion of the water which is chemically bound and does not participate in phase conversions.

The effect of the porous aggregate on the ice content of concrete was determined to more fully expose the cryologic characteristic. Studies were conducted to determine the phase state of water in cement paste of normal thickness (23.75%), water of composition 1:3 at  $W/C = 0.45$  and grade 200 algoporite concrete at  $W/C = 0.58$ . All these test samples were also produced from Belgorod alite ( $3\text{CaO} \cdot \text{SiO}_2 = 64\%$ ) low aluminate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 = 4\%$ ) grade 400 portland cement. In this case the freezing was implemented immediately after preparing the samples and at age 24 hours.

Tests have shown that the amount of ice formed in cement paste, mortar, light and weighted concrete when freezing them immediately after manufacture is respectively: at  $-2^{\circ}\text{C}$  80, 85, 90 and 85%; at  $-3^{\circ}\text{C}$  89, 92, 94 and 89%; at  $-10^{\circ}\text{C}$  98, 96, 96 and 94%; at  $-38^{\circ}\text{C}$  96-98%.

The amount of ice formed in these same samples cured before freezing for 24 hours under normal conditions drops considerably; it is respectively: at  $-3^{\circ}\text{C}$  50, 57, 70 and 62%; at  $-5^{\circ}\text{C}$  62, 74, 74 and 74; at  $-10^{\circ}\text{C}$  63, 75, 75 and 78; at  $-38^{\circ}\text{C}$  68, 79, 80 and 83%. It may be noted that alaporite concrete freezes more rapidly than crushed limestone concrete.

At temperatures down to  $-2^{\circ}\text{C}$  water in freshly made concrete is for some time in a supercooled state; at  $-1^{\circ}\text{C}$  in these tests, as in those described previously, approximately 80% of the water is still in the liquid phase.

A comparison of ice content in cement paste freshly made and after curing test samples of it for 24 hours under normal conditions is of indubitable interest. The results of determining the amount of ice in cement paste and cement stone after 24 hours of hardening are shown in Figure 1.3. In this case the same portland cement from a Belgorod factory was used.

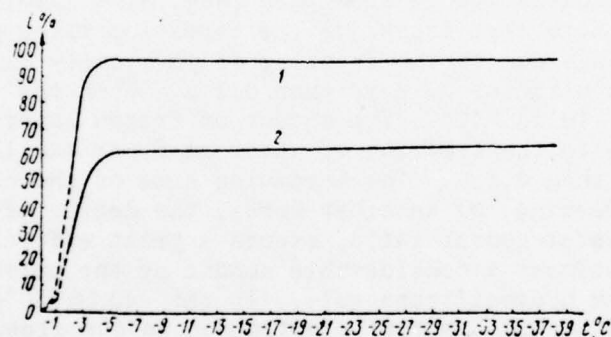


Figure 1.3. Change in Ice Content of Cement Paste. 1, In a newly made state; 2, At age 24 hours.

As can be seen from the figure, as the temperature drops the amount of ice increases. In this case in samples frozen during the first hours, most of the water becomes ice at a temperature below  $-2^{\circ}\text{C}$ , and in samples frozen after 24 hours of normal hardening at a temperature of  $-5^{\circ}\text{C}$ .

Intensive ice formation takes place in this temperature range due to the freezing of physically-mechanically bound water in pores with radius more than  $0.1 \mu$ . When the temperature drops further from  $-10$  to  $-38^{\circ}\text{C}$ , the amount of frozen water increases insignificantly due to freezing of it in capillaries with a diameter of less than  $0.1 \mu$ . The hardening of concrete before the beginning of freezing, or in other words, the degree of cement hydration and water cement ratio, exerts a great effect

on ice content. In our tests cement samples were prepared from a paste of normal thickness.

All this stated about the kinetics of phase changes in the freezing and thawing process of water is the cause of the cement hydration process and concrete hardening at sub-zero temperatures. Hydration and liberation of heat by cement associated with it as well as the hardening of concrete in freezing weather are due to the water contained in it in the liquid phase.

Analysis of data from numerous tests with cement paste, mortar and concretes of various aggregates in a sufficiently large temperature range make it possible to explain in a quite definite scientific manner the hardening processes which occur at sub-zero temperatures.

Theoretical precepts are only then valid when they are based on reliable experimental data. Based on data presented and their interpretation we can draw conclusions not only of a general nature, but also use them for practical purposes. However, it should be noted that the solution to the problems associated with selecting a production method and with estimating concrete strengthening at variable above zero and sub-zero temperatures remains a very complex task. A whole series of factors must be considered in each individual case.

— The transition of water from a liquid state into a solid state occurs with crystallization, during which heat is liberated. The viscosity of water at  $0^{\circ}\text{C}$  becomes 1.8 times greater than at  $20^{\circ}\text{C}$  and 6 times greater than at  $100^{\circ}\text{C}$ .

— As the temperature drops, the movement of water molecules is retarded and they aggregate. The chemical activity of water drops. A number of anomalous phenomena are noted which are very difficult to study even using modern research methods (chemical and petrographic analyses, ultrasonics, deformations, x-ray analysis). When the temperature of water drops below  $0^{\circ}\text{C}$ , transition of it into a solid state is not immediately observed. As the result of the increase in the viscosity of water as the temperature drops and its being contained in capillaries of variable cross-section, it remains in a supercooled state for some time, i.e., remains in the liquid phase below the critical point.

Tests confirm that a supercooled state precedes the beginning of crystallization of water solutions in the free state as well as in concrete even when mixing cement using fresh water.

As can be seen from Figure 1.4, in the experiments of E. Kh. Bulgakov [8] slag portland cement mortar began to freeze after 20-40 minutes in the supercooled state at temperatures of  $-4$  and  $-6^{\circ}\text{C}$ . However, during a short time the temperature remained below  $0^{\circ}\text{C}$  due to the heat of crystallization of the ice and the dissolving of the salts contained in the cement. It was established in these same experiments that the addition of chlorine salts and sodium nitrite reduced the temperature of the supercooled state  $3^{\circ}$  compared to the cryoscopic point at this concentration.



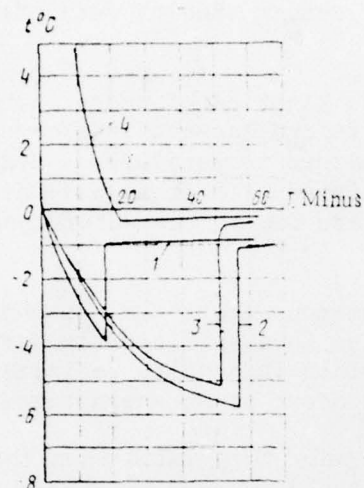


Figure 1.4. Freezing Curves of Samples at Various Ambient Temperatures. 1,  $t = -4^{\circ}\text{C}$ ; 2,  $t = -5.8^{\circ}\text{C}$ ; 3,  $t = -5.2^{\circ}\text{C}$ .

Various opinions have been repeatedly given on the effect of the type of water used for making concrete on its physical-mechanical properties. In this case they have not always been associated with the hardness of the water and the content of dissolved substances. D. Kh. Bulgakov [8] proposed the hypothesis that water boiled for 2-3 hours ensures increased strength in slag portland cement concrete and samples prepared from mineral 2  $\text{CaO} \cdot \text{SiO}_2$ , and conversely reduces concrete strength in bauxite cement and samples made from mineral 3  $\text{CaO} \cdot \text{SiO}_2$ . E. Kh. Bulgakov explains this dependency by the effect of thermally treated tap water on the change in the structure of the water molecules.

It was decided that a careful experimental check of this hypothesis be conducted. The check was carried out on three basic types of cements using various types of water for making the concrete: ordinary tap water boiled for 2-3 hours, distilled water and water obtained from melted ice. After boiling the water was cooled to the ambient temperature. Concretes of two compositions were made using 320 and 600  $\text{kg/m}^3$  cement. The first composition contained 185 l of water at  $\text{W/C} = 0.58$ , the second 224 l of water at  $\text{W/C} = 0.38$  per cubic meter of concrete. Slumping of the cone varied within 0-1.5 cm, and stiffness 15-25 s. Stiffer mixtures were produced using 320  $\text{kg/m}^3$  cement.

For the first days the sample cubes were kept in metallic forms  $10 \times 10 \times 10$  cm, and then dismantled and transferred to a normal storage chamber. Compression strength tests were conducted after 3, 7, 28 and 60 hours of normal hardening. At the same time samples of standard mortar were prepared with spreading of the cone 105-107 mm. The water-cement ratio using various cements varied within 0.4-0.45.

The results of compression tests on concrete samples and bending tests on mortar samples at 7 and 28 days are shown in Table 1.2. As can be seen from the results (Table 1.2), the hypothesis concerning the effect of thermally treated water on the strength of concrete and mortar prepared using various cements was not confirmed. At age 7 days in slag portland cement and bauxite cement concretes the strength was 9 and 13% greater when using boiled water. For portland cement it was 15.5% less than in concrete mixed using ordinary tap water. And at age 28 days the strength of portland cement and slag portland cement concrete was 5.5-8.4% less when using the same boil of water. In testing samples at age 60 days all the indicators of strength of these concretes converged. The limits of the deviations in strength indicators did not exceed the usual 5-15%.

As observations have shown when preparing the samples, the effect of certain inaccuracies in conducting the tests did affect the variations in strength to a large degree. Nor can any definite conclusions be drawn with regard to using distilled water and water from melted ice. In portland cement and bauxite cement mortars some drop in strength at age 7 and 28 days is generally noted, and in slag portland cement mortar strength was 6-12% higher only at age 7 days. By age 28 days it was somewhat lower than in mortar prepared using ordinary tap water.

Distilled water, as it is softer, did not promote an increase in the diffusion of the mortar cone at the same W/C for various compositions. Therefore the water requirement of the concrete mixture at the same consistency did not need to change. Thus, the effect of thermal treatment of water on concrete strength was not shown in the experiments.

The problem of the effect of the type of water on the properties of concretes mixed with them is more complex than it seems to certain technologists.

Many works have been published during the last 5-6 years on increasing the strength of concrete mixed with water which has been magnetically treated. Laboratory studies were conducted in the Moscow State University, Novocherkassk, Permsk, Krasnodarsk and other polytechnical institutes, in the Minsk Institute of Heat and Mass Exchange, in the Central Scientific Research and Planning Institute of Standard and Experimental Planning of Housing, the Scientific Research Institute of Concrete and Reinforced Concrete, in the Institute of Mining-Chemical Raw Materials and others. However, the theory of the action of an electromagnetic field on the properties of water used in mixing concrete have not been developed by anyone. Some researchers use magnetic water in conjunction with other technological factors. For example, service active substances are added to concrete, water is saturated with iron ions, repeated vibration is used, natural sand-gravel heterogenous mixtures are used instead of fractionated aggregates and so forth.

TABLE 1.2. STRENGTH OF CONCRETE AND MORTAR MIXED USING DIFFERENT TYPES OF WATER

Cement	Type of mixing water	Strength				W/C mortar	Mortar setting times	
		Compressed conc.		Bending mortar			Begin	End
		Age, days						
		7	28	7	28			
Slag portland cement	Tap	$\frac{14,2}{100}$	$\frac{33,2}{100}$	$\frac{2,85}{100}$	$\frac{6,64}{100}$	0,45	2 h 01 min	5 h 41 min
	Boiled	$\frac{15,5}{109}$	$\frac{30,4}{91,6}$	$\frac{3,19}{112}$	$\frac{5,76}{87}$	0,45	1 h 53 min	5 h 28 min
	Distilled	$\frac{16,1}{113}$	$\frac{31,1}{93,8}$	$\frac{3,03}{106}$	$\frac{6,56}{99}$	0,46	2 h 03 min	5 h 39 min
	From melted ice	$\frac{14,3}{100,7}$	$\frac{28,8}{86,7}$	$\frac{3,04}{106,8}$	$\frac{5,51}{83}$	0,45	1 h 50 min	5 h 30 min
Belgorod Factory portland cement	Tap	$\frac{36,8}{100}$	$\frac{52,7}{100}$	$\frac{5,37}{100}$	$\frac{7,79}{100}$	0,4	2 h 43 min	6 h 20 min
	Boiled	$\frac{31,1}{84,5}$	$\frac{50,4}{95,5}$	$\frac{4,8}{89,5}$	$\frac{7,6}{97,6}$	0,4	3 h 04 min	6 h 07 min
	Distilled	$\frac{35,4}{96,4}$	$\frac{49,6}{94,3}$	$\frac{4,84}{90}$	$\frac{7,38}{95}$	0,4	2 h 50 min	6 h 15 min
	From melted ice	$\frac{36,8}{100}$	$\frac{49,4}{93,7}$	$\frac{5,29}{98,5}$	$\frac{7,11}{91,4}$	0,4	2 h 55 min	6 h 07 min
Bauxite	Tap	$\frac{33,5}{100}$	$\frac{41,4}{100}$	$\frac{5,52}{100}$	$\frac{4,99}{100}$	0,44	1 h 10 min	3 h 40 min
	Boiled	$\frac{38}{113}$	$\frac{48,5}{117}$	$\frac{4,85}{88}$	$\frac{4,54}{91}$	0,44	1 h 04 min	3 h 22 min
	Distilled	$\frac{34}{101}$	$\frac{43,4}{105}$	$\frac{4,96}{90}$	$\frac{4,76}{95,6}$	0,45	1 h 07 min	3 h 07 min
	From melted ice	$\frac{37,7}{112,5}$	$\frac{42,3}{102}$	$\frac{4,97}{90,2}$	$\frac{4,66}{93,6}$	0,44	1 h 02 min	3 h 25 min

NOTE. Numerator shows compression and bending strength in MPa; denominator % strength of strength of concrete mixed using ordinary tap water. Commas indicate decimal points.



Studies conducted by the Scientific Research Institute of Concrete and Reinforced Concrete and certain other organizations have shown that magnetic water does not directly affect concrete strength. An increase in the workability of stiff mixtures, mainly lightweight aggregate concrete ones, was noted under certain magnetic water treatment conditions.

It should be emphasized that most researchers have confirmed the concomitant increase in concrete strength with magnetic water without reducing the water-cement ratio. That is, the effect of plastification of the mixtures (if there were such) was not used in their experiments and the consumption of magnetically treated water was not reduced compared to using ordinary tap water. With regard to concrete technology the processes of magnetic treatment of water cannot be controlled nor monitored. Properties of water may change not only seasonally, but also during a single day. Cement consumption in construction must be reduced by other scientifically sound measures. Therefore the use of magnetic water for mixing cement under industrial conditions should be foregone. The manuals and temporary instructions devolved by a number of organizations for industrial use of magnetic water when mixing concretes are premature, since they are not substantiated.

## CHAPTER 2

### HYDRATION, HEAT LIBERATION AND STRUCTURE OF NEW FORMATIONS DURING CEMENT HARDENING UNDER VARIED TEMPERATURE CONDITIONS

The processes associated with the hydration of portland cement have been studied for more than 100 years in many countries. A number of hypotheses (theories) about the hydration processes of cement minerals and about its hardening with time have been proposed. However, none of the hypotheses, including those of A. Le. Chatelier, V. Michaelis, A. A. Baykov, P. A. Rebindr, L. Forsen, T. Powers, H. Taylor and others is universally accepted as the theory of hardening. This is confirmed by recent studies using modern instruments and methods. Knowledge of the mineralogy of cement clinker is thoroughly known, and the role of physical and physical-chemical processes in hardening under varied temperature conditions has been explained.

Discussions on the question of the hydration mechanism and cement hardening have been conducted for the last 10-12 years among leading scientists in the Soviet Union and abroad. Some assert that hardening occurs only by the products of supersaturated solutions dissolving and crystallizing out. Others believe that the products of new formations are the result of topochemical reactions. The third group (including the author) believes, without excluding topochemical reactions, that hardening processes begin and proceed basically by the dissolving and crystallizing out of products of hydration and hydrolysis from supersaturated solutions.

Without comparing these hypotheses there is reason to assume that the processes of hydration and cement hardening begin with hydrates dissolving and crystallizing out. Then, as time passes, molecules of water and ions of OH are introduced into the crystal lattice of the minerals of the non-reacted portion of the cement clinker without passing through solution. With limited passage of water through the dense envelopes of the gel, cement hydration slowly intensifies topochemically, i.e., by direct interaction of the minerals with water without the products of the new formations passing into solution. Water diffuses through the ultramicropores of the gel, especially when it is recrystallized.

Ideas of purely colloidal processes, similar to the thickening and solidification of glue, have been refuted by modern study methods, x-ray structure, electron microscopic and others, even with regard to the early stage of hardening. It has been established that calcium hydrosilicates are simply concretions of extremely fine crystals, although they exhibit properties characteristic of gels.

#### Chemical Mineralogical Composition of Cements.

Ordinary determination of the chemical composition of cement does not yield the necessary characteristics of its properties. It is not possible to determine the rate of hardening and establish the most favorable hygrothermal conditions for the curing of concrete composed of

some type of cement from the data of percentage oxide content. The mineralogical content cannot be determined, since factory cements contain various mineral ground admixtures.

The setting and hardening of cements is caused by the interaction of cement with water during which the minerals of the clinker dissolve and are hydrated (affixation of water). Therefore the mineralogical content best characterizes the technical properties of cements.

The mineralogical content of cement predetermines the composition and structure of new formations as well as the strengthening of cement stone in time depending on various factors.

Portland cement clinker contains the following principal minerals: tricalcium silicate  $3\text{CaO}\cdot\text{SiO}_2^*$ , by calcium silicate  $\beta$   $2\text{CaO}\cdot\text{SiO}_2$ , tricalcium aluminate  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  and tetracalcium aluminoferrite  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ . Usually portland cement clinker contains approximately 75% tricalcium and bicalcium silicate. Portland cements containing at least 50%  $\text{C}_3\text{S}$  are recommended for use during winter operations.

Portland cement clinker contains approximately 20% tricalcium aluminate and tetracalcium aluminoferrite. Since they are calcined together with calcium silicates at a high temperature, they then partially change to a glassy mass upon rapid cooling.

Besides those minerals contained in cement clinker, slag portland cement is also made up of the minerals in the slags: bicalcium silicate  $\beta$  and  $\gamma$   $2\text{CaO}\cdot\text{SiO}_2$ , gehlenite  $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  and certain other components. In addition to the neat minerals, a large amount of active silica is present in pozzuolanic cement (tripoli earth, trass and others).

The clinker of bauxite cement contains the following: monocalcium aluminate  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ , monocalcium bialuminate  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , pentacalcium trialuminate  $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$ , tricalcium silicate, gehlenite and others. Bauxite cement usually contains approximately 60% monocalcium aluminate as its principal component. An increased content of pentacalcium trialuminate causes rapid setting of bauxite cement. Gehlenite is an inert component of the cement.

To accelerate the hardening of cements the clinker must be ground very finely since in doing this the specific surface of the powder produced is increased. It is desirable to have cements of which at least

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\*Subsequently the following abbreviations will be used:  $\text{C}_3\text{S}$  instead of  $3\text{CaO}\cdot\text{SiO}_2$ ;  $\text{C}_2\text{S}$  instead of  $2\text{CaO}\cdot\text{SiO}_2$ ;  $\text{C}_3\text{A}$  instead of  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  and  $\text{C}_4\text{AF}$  instead of  $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ .



95% pass through a sieve with 4900 holes/cm<sup>2</sup> or with a specific surface of approximately 4000 cm<sup>2</sup>/g determined using Tovarov's method.

For winter concreting more active cements should be used than under other conditions.

When selecting cements according to a mineralogical criterion it must be kept in mind that the aluminum containing minerals C<sub>3</sub>A and C<sub>4</sub>AF have the greatest effect on the processes of setting and early hardening of portland cement. Hydrosulfoaluminate and calcium hydroaluminate together with calcium oxide hydrate create the crystalline skeleton and determine the initial strength of the cement stone and concrete.

At reduced above-zero and sub-zero temperatures the use of high alite cement with an increased content of C<sub>3</sub>A and C<sub>4</sub>AF is recommended, and during thermal processing of products medium alite cement with a small quantity of aluminum containing minerals.

After the crystalline skeleton is formed from the calcium hydro-aluminates, subsequent development of it and consolidation of the structure, and consequently the strengthening of the cement stone and concrete, occur mainly due to the calcium hydrosilicates.

#### Cement Hydration at Above-Zero Temperatures.

The rate of hardening and final strength of concrete definitely depend on the rate and degree of hydration of the cements used. Soviet and foreign chemists and technologists who study cementing materials and concretes are occupied with the study of the hydration processes of the minerals of cement clinker and various cements. Methods of controlling the setting and hardening processes of concrete under different conditions of use are being sought as the result of the study of the hydration process of cements and the components of their minerals. In doing this requirements for the technical properties of cements are being developed.

It must be noted that studies conducted in this area are basically limited to studying hydration at normal and increased temperatures, including during autoclave processing which is used on a small scale in practice. By citing certain data for the characteristics of hydration of individual materials and portland cement at above-zero temperatures, we will examine in somewhat more detail the results of our studies on cement hydration at low above-zero and at sub-zero temperatures.

At present the problem of studying cement hydration and concrete hardening at sub-zero temperatures is quite timely. Complete clarity must be achieved with regard to the intensity of concrete hardening at zero and sub-zero temperatures. For the time being these few results of experimental studies at sub-zero temperatures should direct the attention of scientists to their further development, to the necessity of thoroughly studying the physical chemical processes which occur in concretes during winter concreting.

Heretofore researchers have mostly studied the action of early freezing on the physical mechanical properties of concretes and devoted a great deal of attention to the resistance of concrete to freezing. Abroad and in the USSR few studies have been devoted to the physical and chemical properties of winter concrete and its cryological characteristics.

In conducting experiments and in examining the results obtained in studying the hydration of portland cements with various methods (chemical analysis, x-ray structure analysis, microscopy, weight differential thermal analysis), we have been faced with many methodological questions in terms of the technique itself of preparing samples. In conjunction with this a number of analyses have been repeated and the care with which all operations are executed has been increased. Therefore it is appropriate here to mention the statement of L. Copeland, D. Cantro, G. Verbek [24] in the introduction of the report "Chemistry of Portland Cement Hydration" at the Fourth International Congress on Cement Chemistry: "The difficulties which arise in studying the chemistry of portland cement hydration have been repeatedly discussed, but they are well-known only to those who work in this field. In spite of this certain successes have been achieved, although the road to understanding the processes of hydration is rather complex." It is even more complex in conducting operations at sub-zero temperatures. There exist no universally accepted standard method for determining adsorbed and hydrate water. Tests show that hydrate water begins to be removed from aluminate components not at 105°C, as many believe, but at 60°C and even lower.

At 105°C adsorptionally bound water may be removed only in the case of inert materials, and not cementing materials. For example, it is quite apparent that at 105°C water is removed from sulfoaluminate, and gypsum is dehydrated.

Certain researchers accept a different maximum temperature at which complete losses are detected when calcining samples. Some believe that the water which is removed at 1000°C should be assumed to be chemically or strongly bound water, others at 600°C or 700°C. The boundaries which divide chemically (strongly), adsorptionally (weakly) bound and free waters are very difficult to ascertain. Some of the water may be adsorptionally retained rather strongly in the crystal lattice without being crystallohydrate.

Considering the greater service of the hydration products, the strength of cement stone is created as the result of the combination of physical (adsorption) forces, the so-called Van der Waals forces, with chemical forces, the bonds of which are called valent.

The closer the contact between the solid particles and the monomolecular layer of adsorbed water, the more strong are their bonds. As they recede, their bonds weaken. Water is in large part in the free state in large pores. For example, it can be easily observed how water is freely eliminated from the cells (large pores) of cellular or porous concrete. Free water does not increase, but conversely, decreases the strength and softens the cement stone and concrete.

The hydration of the individual minerals of portland cement can be characterized by the results of the studies of Professor V. N. Yung conducted at the D. I. Mendeleyev Moscow Chemical-Technological Institute (Table 2.1).

The quantity of chemically bound water (in percentages of cement mass) was determined at age 3, 7, 28, 180 days and with complete hydration under normal conditions. In addition, a similar determination was conducted after steam curing under pressure of 0.8 MPa in an autoclave for 8 hours.

Of all the minerals, tricalcium aluminate hydrates most rapidly. Tetracalcium aluminoferrite also hydrates rather rapidly. Calcium silicates hydrate considerably more slowly. Bicalcium silicate hydrates especially slowly; at age 3 days it affixes only approximately 1%, and at age 1 month 2.5% of the water.

As the result of 8 hour autoclave treatment the minerals of portland cement clinker affects almost as much water as in 180 day storage.

TABLE 2.1. QUANTITY OF WATER AFFIXED BY INDIVIDUAL MINERALS, % OF CEMENT MASS

Minerals	Hardening conditions					
	Normal, during days				With complete hydration	After steam treatment under a pressure of 0.8 MPa in a regime of 2 - 8 - 2 hours
	3	7	28	180		
C <sub>3</sub> A	19	22	25	30	35	23
C <sub>4</sub> AF	14	16	18	22	29	20
C <sub>3</sub> S	5	7	10	13	16	12
C <sub>2</sub> S	1	1.5	2.5	5	10	5

Commas indicate decimal points.

The degree of hydration of the neat minerals of portland cement, beginning from the instant of mixing the cement paste with W/C = 0.5 to 91 days of curing at a temperature of 20°C, is shown in Table 2.2, according to the data of G. Yamagushi.

The minerals are distributed by degree of hydration in the same sequence as by quantity of bound water. As the studies of S. D. Okorokov have shown, the presence of gypsum and the interaction of portland cement hydration products during hardening somewhat changes the rate of hydration of the minerals and cement compared to individual minerals. The water cement ratio affects the rate and degree of hydration of minerals as well as cements. Finer grinding increases the hydration rate, especially during the initial period. As the temperature increases, the rate of hydration increases. The degree of hydration does not increase with the passage of time, but according to the data of a number of researchers somewhat decreases. As can be seen from the works of S. Brunauer and D. Kantro [7], the degree of hydration of calcium silicates in paste with a W/C = 0.70 at



temperatures 5, 25 and 50°C varies considerably in time (Figure 2.1). At age 300 days the degree of hydration of bicalcium silicate equalizes at all three temperatures.

TABLE 2.2. DEGREE OF HYDRATION OF PORTLAND CEMENT MINERALS

Mineral	Degree of hydration, % in age				
	3 min	1 hour	1 day	28 days	91 days
$C_3S$	1-4	1-9	40-70	80-100	90-100
$\beta-C_2S$	0.5-1	1-2	7-15	20-35	75-80
$C_3A$	10-30	14-32	40-60	60-80	85-95
$C_4AF$	8-20	11-23	20-40	50-70	80-85

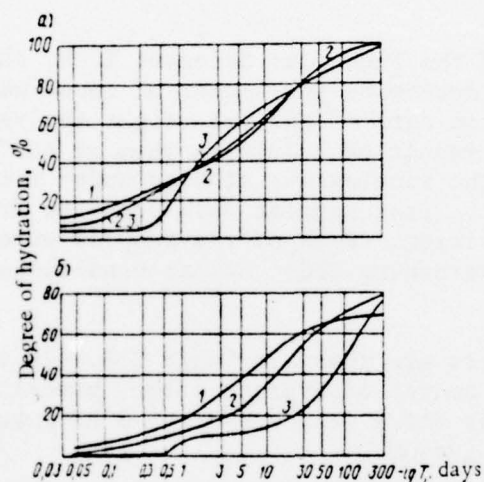


Figure 2.1. Degree of Hydration of Cement in Paste at  $W/C = 0.7$ .  
a, For  $C_3S$ ; b, For  $\beta C_2S$ ; 1, At  $t = 50^\circ C$ ;  
2, At  $t = 25^\circ C$ ; 3, At  $t = 5^\circ C$ .

The highest indices were observed in tricalcium silicate at this age at a temperature of 25°C and some reduction in the degree of hydration is noted at a temperature of 50°C. At a temperature of 5°C retardation in the degree of hydration is observed only in the initial stage. In the final analysis we may consider that at 5°C calcium silicates hydrate with time to the same depth as at 25°C. The authors explain this by the fact that as the temperature drops, a more permeable envelope of the products of the new formations around the cement particles is formed than at increased temperatures [7].

Although aluminum containing minerals rapidly hydrate and bind the largest amount of water, at increased temperatures they reduce the strength of the cement stone.

Experimental data on the rate and degree of hydration of cements at different temperatures is of great interest for technologists and concrete workers. Of the cements, bauxite cement containing predominantly calcium aluminates hydrates most rapidly. A grade of bauxite cement with a diameter of 50  $\mu$  is almost completely hydrated by age 3 days.

Portland cement hydrates second most quickly. The more the basic the calcium silicates and the more finely the portland cement is ground, the more rapidly it hydrates. Tests show that a grain of grade 400-500 cement with a diameter of approximately 10  $\mu$  is completely hydrated by age 28 days. At age one month ordinary portland cement of this activity affixes approximately 12% of the water, and at full hydration 20-25%. High aluminate portland cement chemically binds approximately 30% of the water as the result of the forming calcium sulfoaluminate affixing a larger quantity of water.

The author, Candidate of the Technical Sciences Z. M. Larionova, and Engineer S. Kh. Yarlushkina determine the amount of bound water in hydrated new formations calculated from data of thermal weight analysis and from mass loss of samples as the result of calcining them at 600°C. At the same time the structure of the samples was studied under a microscope and in terms of water absorption. Test samples were prepared from cements of various mineralogical composition. Some of the samples were tested for compression strength after hardening under normal conditions for 1, 3 and 28 days.

The results of the studies are shown in Table 2.3. It contains data on the degree of hydration, amount of hydrate water, porosity and compression strength of samples of cement stone with a W/C = 0.3 of pure neat cements without admixtures and with gypsum.

Alite high aluminate clinker was composed of:  $C_3S = 66\%$ ;  $C_2S = 9\%$ ;  $C_3A = 14\%$ ;  $C_4AF = 5\%$ , and alite low aluminate differed by the content of  $C_3A = 2\%$  and  $C_4AF = 16\%$ . The samples were hardened under normal conditions. Addition of gypsum accelerates clinker hydration during the first days. A more considerable acceleration is observed in a case of mixing low activity low aluminate clinker. Hydration of high aluminate neat cement is accompanied by the formation of a large number of hydroaluminate and hydrosilicate compounds.

In normally hardened samples the hydrosilicate mass has a micro-crystalline structure; foliated crystals of  $C_2H_2$  can only be distinguished in low-density sections of the cement stone using an electron microscope. Cement stone of low aluminate clinker is distinguished by a low degree of hydration and low density structure in the first days of hardening.

To study the effect of steam curing on the processes of hydration and structural formation, samples of cement stone and concrete were prepared using alite high aluminate cement from grade 400 clinker from the

Voskresensk Factory ( $C_3S = 49\%$ ;  $C_2S = 21\%$ ;  $C_3A = 12\%$ ;  $C_4AF = 14\%$ ). All samples were prepared with a  $W/C = 0.4$ . The concrete, mixed using quartz sand and crushed limestone, was assumed to have a composition 1:1:2.2. Steam curing was carried out at  $80^\circ C$  according to a regime 2 + 3 + M + 2 hours. The time (N) of isothermal heating was equalized to 2, 6, 12 and 16 hours. The results of the experiments are shown in Table 2.4.

TABLE 2.3. HYDRATION AND PROPERTIES OF PURE NEAT CEMENTS

Cements	Sample age, days	Degree of hydration, %		Amount of hydrate water, %		Microscopic porosity, %	Compression strength, MPa
		By the amount of non-hydrated alite	By the amount of non-hydrated cement	By data of thermal weight analysis	by data of chemical analysis		
Alite high aluminate	1	32	31	10	8.5	2.6	4.4
	3	56	51	14	14	1.3	—
	28	72	66	17.5	18	1	32.5
Alite high aluminate with 5% $CaSO_4$	1	36	35	11	—	2.3	4.9
	3	55	53	14	—	1.2	—
	28	72	67	18	—	0.9	34.4
Alite low aluminate	1	19	18	5	6	2.3	2.8
	3	46	40	8	10	1.2	—
	28	64	57	16	17	1.1	32.2
Alite low aluminate with 5% $CaSO_4$	1	28	26	8	—	2.1	3.3
	3	57	51	13	—	1.1	—
	28	70	63	17	—	0.8	33.3

Commas indicate decimal points.

At age 28 days the amount of hydrate water during normal hardening dropped compared to the data shown in Table 2.3, i.e., 15% instead of 16-18%. After steam curing the indices of the quantity of hydrate water and degree of hydration in percent were higher compared with indices after 28 days of storing the samples only under normal conditions. However, the strength in steam cured samples was clearly lower than that in samples stored for the entire period under normal conditions.

The porosity of the steam cured samples was greater than that of those hardened under normal conditions. At the same time it was noted that as the length of the period of isothermic heating increased, the concrete consolidated and the state of the contacts with aggregates improved. After 12 hours of steam curing the strength did not increase, but conversely, decreased. This question will be subsequently examined in more detail with the explanation of the progressive decrease in strength. In analyzing the results shown in Table 2.4 it should be kept in mind that in this case the portland cement was high aluminate.



V. M. Rossovskiy of the All Union Scientific Research Institute of Industrial Technology of Precast Reinforced Concrete Structural Parts and Products conducted interesting studies on cement hydration during normal hardening, steam curing and preliminary electric heating of the concrete mixture. He studied samples made of portland cement from the "Gigant" Factory and the Belgorod Factory. Special equipment was built to study hydration using Dewar flasks and exsiccators in which thermal treatment was conducted. The results of determining the amount of bound water depending on hardening conditions for portland cement from the Belgorod Factory are shown in Table 2.5.

TABLE 2.4. HYDRATION AND PROPERTIES OF CEMENT STONE AND CONCRETE OF PORTLAND CEMENT FROM THE VOSKRESENSK FACTORY

Samples	Hardening Conditions	Sample age, days	Period of isothermal heating N, hrs.	Degree of alite hydration, %	Amount of hydrate water, %	Porosity in terms of water absorption at age 28 days, %	Compression strength, MPa
Cement stone W/C = 0.4	Normal hardening	1 28	—	28	9	—	4.4
			—	68	15	—	41.3
	Steam curing at 80°C according to the regime 2 + 3 + N + 2 hrs.	After steam curing	2	53	14	—	27.8
			6	70	15	—	32.2
			12	78	16	—	33.2
			16	79	16.5	—	29.1
Concrete 1:1:2.2, W/C = 0.4	Normal hardening	1 28	—	—	—	—	5.2
			—	—	—	4.6	27.6
	Steam curing at 80°C according to the regime 2 + 3 + N + 2 hrs.	After steam curing	2	—	—	5.2	16.5
			6	—	—	5.4	24.9
			12	—	—	5.2	29.2
			16	—	—	5.6	21.6

Commas indicate decimal points.

In contrast to the data cited for the Belgorod portland cement, the quantity of bound water in samples using portland cement from the "Gigant" Factory was somewhat higher, and what is most important, it was more intensely bound during the earlier periods. In the initial periods the content of bound water and the degree of hydration were 1.5-2 times higher than in cement from the Belgorod Factory. By age 28 days this difference had increased from 5 to 15%. Complete hydration of portland cement from the "Gigant" Factory is characterized by 26.36% instead of 22% in the portland cement from the Belgorod Factory.

TABLE 2.5. EFFECT OF HARDENING CONDITIONS ON HYDRATION OF PORTLAND CEMENT FROM THE BELGOROD FACTORY

Time of sampling	Hardening conditions									
	Normal hardening		Steam curing (3 + 8 + 3) hours at 85°C		Prelim. electric heating of mixture at temperature, °C					
	Content of bound water, %	Degree of hydration, %	Content of bound water, %	Degree of hydration, %	50		70		90	
	Content of bound water, %	Degree of hydration, %	Content of bound water, %	Degree of hydration, %	Content of bound water, %	Degree of hydration, %	Content of bound water, %	Degree of hydration, %	Content of bound water, %	Degree of hydration, %
Immed. after heating	—	—	—	—	0,345	1,6	0,787	3,6	1,348	6,1
1 hour	0,451	2,4	—	—	1,326	6	2,261	10,4	3,051	13,9
3 hour	0,653	3	3,423	15,6	3,251	14,8	4,482	20,4	5,646	25,6
6 hour	1,928	8,8	—	—	5,953	27	7,751	35,2	8,551	38,9
12 hour	3,935	17,9	10,405	47,3	8,831	40,1	9,92	45,1	10,161	46,1
1 day	6,682	30,4	10,504	47,7	9,531	43,3	10,616	48,2	11,452	52
3 days	10,752	49	11,071	53,3	11,552	52,5	12,548	57	13,011	59,1
7 days	13,254	60,2	11,85	54	13,671	62,1	12,91	58,7	14,261	64,8
14 days	15,357	70	12,74	58	15,123	68,8	14,299	65	14,949	68
28 days	17,701	80,5	14,244	65	17,251	78,4	16,655	75,7	15,741	70,3
12 months	20,501	93	17,069	73	19,884	90,4	18,747	85	16,71	76

Note. Complete hydration - 22.02%.  
Commas indicate decimal points.

In the first hours water is primarily chemically bound during electric heating. In doing this the higher the heating temperature, the more quickly hydration of the cement proceeds. However, beginning at age 4-5 days a tendency is observed to increase the amount of bound water in samples with lower electric heating temperatures. By age 2-3 days in portland cement from the "Gigant" Factory and by approximately age 3-7 days in portland cement from the Belgorod Factory stored under normal hardening conditions the amount of chemically bound water becomes the same as in portland cements hardened under accelerated conditions. Subsequently a tendency to reduction of the amount of chemically bound water is observed in thermal treatment.

To conclude the analysis of these data it may be stated that there is no unified opinion among researchers with regard to the depth and degree of hydration of cements during thermal treatment compared to normal hardening. For example, in comparing chemically bound water in the two cements examined it should be kept in mind that portland cement from the "Gigant" Factory is characterized by finer grinding (4100 cm<sup>2</sup>/g) and increased aluminate content, and portland cement from the Belgorod Factory was more coarsely ground (2850 cm<sup>2</sup>/g) and contained little aluminate. Often comparability criteria are lacking in the examination of the data of various researchers. Nevertheless it can be stated with certainty that a general characteristic has been established with regard to the effect of different temperatures

on the processes of cement hydration. The data cited by us will aid in orientation in questions of selecting cements and concrete hardening conditions at above zero temperatures.

#### Hydration of Cement at Sub-Zero Temperatures.

As was noted, the effect of various above zero temperatures on the rate and degree of hydration of cement has been studied by many scientists, and the results of their studies have been reported at international congresses on cement chemistry and are cited in many Soviet and foreign works.

In spite of the great deal of scientific and practical interest, the question of the effect of sub-zero temperatures on the kinetics and degree of hydration of cement has been studied very little and is poorly treated in the literature. In conjunction with this special studies have been conducted in the laboratory for methods of accelerating concrete hardening of the Scientific Research Institute of Concrete and Reinforced Concrete which were directed at the study of phase transformations of the liquid phase, the kinetics of the binding of water and heat liberation by cement as well as the strengthening of cement stone, mortar and concrete at sub-zero temperatures which occurs at the same time.

It is known that the quantity of volatile water and degree of hydration of minerals as well as the amount of evolvable exothermic heat are a result and a measure of the degree of cement hydration at various temperatures with the passage of time.

The account given in the first chapter about the kinetics of phase changes in the water freezing and melting process is the cause, and hydration and heat liberation of cement in freezing weather are the result of water contained in the liquid phase. The rate and degree of cement hydration has been studied by the author and L. A. Belova using various methods: x-ray diffraction quantitative analysis, chemical analysis of the quantity of non-hydrated  $C_3S$ , by measuring mass loss when calcining samples at 600 and 1000°C which were first desiccated at 105°C, from the amount of strongly bound water, differential thermal analysis with simultaneous determination of mass loss within the limits of the dehydration effect of  $Ca(OH)_2$  and overall mass loss at 1000°C, and using electron microscopy. The studies were conducted on samples measuring  $2 \times 2 \times 2$  cm prepared from a paste of normal thickness.

The samples were frozen at temperatures of -2, -5, -10 and -20°C immediately after manufacture and then 3, 6, 9, 12 and 24, and in a number of cases 72 hours after curing under normal conditions.

To determine the degree of hydration of cement in freezing weather the samples were cured for 28 days at the corresponding sub-zero temperature, then pulverized and treated with 100% alcohol in a cooling chamber. Some of the samples frozen at the temperatures indicated above and for the same periods of time were cured in freezing weather for 7 and 28 days, then thawed and hardened 28 and 90 days under normal conditions. After-



wards they were also pulverized, treated three times with 100% alcohol and twice with ether, and the degree of cement hydration in them was determined. At the same time normally hardened samples were studied.

The test samples were first sifted through a sieve with 10,000 holes per  $\text{cm}^2$  for x-ray analysis and differential thermal analysis, and through a sieve with 4,900 holes per  $\text{cm}^2$  for chemical analysis. Calcining losses were determined at 600 and 1000°C after desiccation and weighing at 105°C.

Qualitative and quantitative x-ray analyses were conducted using x-ray machine URS-50IM. Quantitative determinations were conducted at the State All Union Scientific Research Institute of the Cement Industry and at the State Scientific Research Institute for Asbestos, Mica, Asbestos Cement Products and for the Planning of Construction of Mica Industry Enterprises by B. P. Ryazin and G. S. Morgolina, and qualitative determinations at the laboratory for physical-chemical studies of the Scientific Research Institute of Concrete and Reinforced Concrete.

Thermograms were taken on an AVTU automatic complex unit equipped to record mass loss during heating and at a sample heating rate of 25-30° per minute to more precisely determine the composition of the new formations and to determine the amount of bound water from the samples. These studies were also conducted in the laboratory of physical-chemical studies of the Scientific Research Institute of Concrete and Reinforced Concrete. The amount of strongly bound water was determined by chemical analysis in the laboratory for methods of accelerating concrete hardening by T. A. Baranova.

The following materials were used in the research: cements from the Belgorod and Voskresenskiy Factories, cement clinker minerals  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  and clinkers from the Nikolayevskiy and Spasskiy Factories, the composition and characteristics of which are shown in Table 2.6.

TABLE 2.6. CEMENT CHARACTERISTICS

Material	Normal thickness, %	Specific surface (according to Tovarov) $\text{cm}^2/\text{g}$	Activity of the cement, MPa	Mineralogical content, %			
				$\text{C}_3\text{S}$	$\text{C}_2\text{S}$	$\text{C}_3\text{A}$	$\text{C}_4\text{AF}$
Portland cement from Belgorod Factory	23,75	2500	40,3	64	15	4	14
Portland cement from Voskresenskiy Factory	25,75	4500	46,1	56	16	7	16
Portland cement clinker from the Nikolayevskiy Factory	—	—	—	57	18	10	12
Cement clinker from Spasskiy Factory	—	—	—	56	18	10	11

Commas indicate decimal points.

First let us turn to the results of chemical analysis to determine hydration of Belgorod and Voskresenskiy portland cements at various sub-zero temperatures (see Table 2.7). This table shows data on the degree of hydration which were obtained by x-ray diffraction analysis, as will be examined later. This comparison is interesting in that the samples studied were from a series of the same samples which underwent chemical analysis. These results were obtained on samples cured at sub-zero temperatures for 28 days and studied immediately after thawing. Before the analysis the samples were dehydrated.

Analysis showed that the interaction of cement and water at a normal temperature begins immediately after mixing. Subsequently the amount of chemically (strongly) bound water increases continually. These samples were predried at 105°C. The Belgorod cement contained 1.13% hydrate water before mixing, and the Voskresenskiy 1.3%. When the prepared samples were dried at up to 105°C, some of the hydrate water was vaporized as the result of the incipient dehydration of the calcium sulfoaluminate. When the samples are calcined at 1000°C with liberation of the hydrate water the  $\text{CaCO}_3$  contained in the cement is decomposed, and the mass losses at these temperatures contain the mass of volatile  $\text{CO}_2$ . It should be noted that regardless of the care with which the operations are carried out, chemical analysis does not make it possible to exactly separate the water in accordance with the theoretical classification of it in cement stone. For example, water adsorbed in the crystalline lattice is included in chemically bound water. Therefore we will call water driven off at 105°C weakly bound, and that obtained by calcination at 1000°C strongly bound. Hydrate water retains  $\text{Ca}(\text{OH})_2$ , and the crystalhydrate (calcium sulfoaluminate) water is for the most part weakly bound and easily removed at temperatures above 60°C (from 31 to 12 molecules).

At temperatures below 0°C cement hydration proceeds with diminishing intensity. Thus, at -2°C the amount of chemically bound water was 4% in both portland cements, and at -5°C 1.5%. The degree of hydration also drops accordingly; in the first case from 26 to 7.6%, and in the second from 18.5 to 4.8%. At temperatures of -10°C and below cement hydration in freshly made samples is insignificant, and the results obtained are associated with the procedure of conducting the analyses. A clear intensification of hydration processes is noted in cement paste and concrete frozen for 12-24 hours and longer. Even at temperatures of -10 or -20°C approximately 4-5% of the water is bound instead of 1.5%. In freezing weather new gel formations aggregate which then intensively crystallize out with the onset of above-zero temperatures.

Data on cement hydration in freezing weather in samples tested soon after preparation are in good agreement with results obtained in studying heat liberation of the same cements. It has been established from research carried out in accordance with a general operating program in the Leningrad Polytechnic Institute that at 0°C 59% of the heat of heat liberation at +20°C is released in 10 days. At -10°C the effect of heat liberation in freshly mixed concrete has not been detected at all. When chemical

additives which reduce the freezing point of the liquid phase are introduced, cement hydration and heat liberation occur at lower sub-zero temperatures; this fact is broadly utilized by builders in the Soviet Union in winter concreting.

TABLE 2.7. AMOUNT OF BOUND WATER AND DEGREE OF HYDRATION OF CEMENTS AT VARIOUS SUB-ZERO TEMPERATURES

Above zero curing time before freezing, hours	Temperature, °C	Belgorod cement				Voskresenskiy cement			
		Degree of hydration in terms of hydrated $C_3S$ , %	Amount of bound water from data of chemical analysis, %			Degree of hydration in terms of hydrated $C_3S$ , %	Amount of bound water from data of chemical analysis, %		
			Mass losses at 105°C	Calcining losses at 1000°C	Total losses of weakly and strongly bound water at 1000°C		Mass losses at 105°C	Calcining losses at 1000°C	Total losses of weakly and strongly bound water at 1000°C
0	-2	26	4.96	4.05	9.01	18.5	3.98	4.01	7.99
0	-5	7.6	2.8	1.48	4.28	4.8	2.87	1.52	4.39
0	-10	—	2.58	1.63	4.21	1.3	2.42	1.34	3.76
0	-20	2	2.1	0.64	2.74	1	1.19	1.02	2.21
3	-20	—	2.04	0.6	2.64	—	—	—	—
6	„	—	2.37	0.99	3.36	—	—	—	—
9	„	—	2.66	1	3.66	—	—	—	—
12	„	21.5	4.08	4.35	8.43	—	—	—	—
24	„	30	4.21	4.63	8.84	34	5.93	5.29	11.21
72	„	—	7.12	6.49	13.61	—	—	—	—
24	„	—	—	—	—	80	6.26	5.43	11.69

Commas indicate decimal points.

Samples prepared using the same portland cements were studied by x-ray diffraction analysis for the degree of hydration after 12 and 24 hours and 28 days of normal hardening as well as after freezing at various ages at temperatures of -2, -5, -10 and -20°C.

The results of the studies of this series of samples are shown in Table 2.8. 12 hours after mixing the amount of hydrated  $C_3S$  for Belgorod cement was 10.5%, after 24 hours 19.6%, after 3 days 24%, after 28 days 59.6% and finally after 90 days 64.6%. The degree of hydration of Voskresenskiy cement at age 1 day was 23%, and by age 28 days it increased to 52.6%. As should have been expected, the Voskresenskiy cement containing a high percentage of the aluminat component hydrated somewhat more rapidly at an early age, and by age 28 days some reduction in the amount of hydrated particles was noted in comparison to the Belgorod cement.

Some increase in the degree of hydration of samples exposed to freezing weather immediately after production at a temperature of -5°C and samples cured 28 days at this temperature (in 7.6 of the samples of Belgorod cement and in 4.8% of Voskresenskiy cement) is still observed. A quite



insignificant (2% for Belgorod and 1% for Voskresenskiy cement) increase in the degree of hydration was obtained at  $-10$  and  $-20^{\circ}\text{C}$ . It is apparent from the same table that at  $-2^{\circ}\text{C}$  hydration proceeds considerably more rapidly than at  $-5^{\circ}\text{C}$ ; for Belgorod cement it is 26% and for Voskresenskiy cement 18.5%. This is a considerable value which is in good agreement with results obtained using other research methods.

For the sake of clarity the results of determining the degree of hydration at normal and sub-zero temperatures of portland cement from the Voskresenskiy Factory are shown in Figure 2.2.

TABLE 2.8. EFFECT OF SUB-ZERO TEMPERATURES ON THE DEGREE OF HYDRATION OF CEMENT (FROM X-RAY ANALYSIS DATA)

Hardening conditions	Degree of hydration of cement paste of normal thickness, %	
	Belgorod portland cement	Voskresenskiy portland cement
12 hours of normal storage	10.5	-
24 hours of normal storage	19.6	23
28 days of normal storage	59.6	52.6
Frozen immediately after manufacture, cured 28 days at $-20^{\circ}\text{C}$ and tested immediately after thawing	2	1
Frozen immediately after manufacture, cured 28 days at $-10^{\circ}\text{C}$ and tested immediately after thawing	2	1.3
Frozen immediately after manufacture, cured 28 days at $-5^{\circ}\text{C}$ and tested immediately after thawing	7.6	4.8
Frozen immediately after manufacture, cured 28 days at $-2^{\circ}\text{C}$ and tested immediately after thawing	26	18.5
Frozen 12 hours after manufacture, cured 28 days at $-20^{\circ}\text{C}$ and tested immediately after thawing	21.5	-
Frozen 24 hours after manufacture, cured 28 days at $-20^{\circ}\text{C}$ and tested immediately after thawing	30	34
Frozen 24 hours after manufacture, cured 28 days at $-5^{\circ}\text{C}$ and tested immediately after thawing	-	40

The figure shows the kinetics of cement hydration at normal temperature with some acceleration in the first days after thawing. By age 28 and 90 days the degree of hydration of these samples was somewhat lower than in samples which were normally hardened. In conjunction with this a special control test was conducted, the results of which will be cited later. The effect of the moisture conditions of curing the samples during prolonged storage was carefully checked.

Concurrent with determining the amount of bound water by chemical analysis, water loss was determined by differential thermal analysis, by calcining samples at  $1000^{\circ}\text{C}$  which had been dehydrated 3 times with 100% alcohol and then treated with ether and dried at  $105^{\circ}\text{C}$ .

The samples under study were manufactured using the same Belgorod and Voskresenskiy cements.

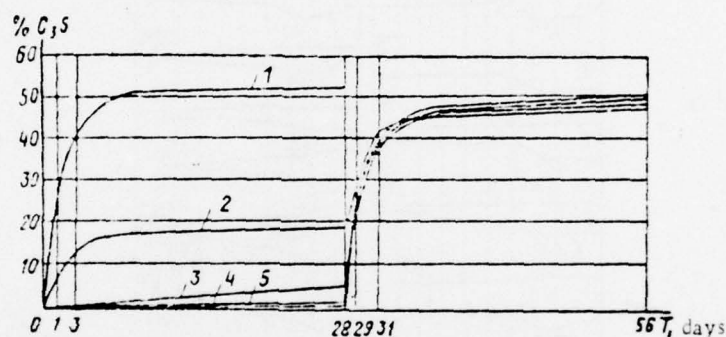


Figure 2.2. Kinetics of Hydration of Voskresenskiy Portland Cement Under Different Temperature Conditions After Freezing and Subsequent 28 Day Hardening Under Normal Conditions. 1, Hardening 28 days under normal conditions; 2, 3, 4, 5, Freezing 28 days at temperatures  $-2$ ,  $-5$ ,  $-10$ ,  $-20^{\circ}\text{C}$  respectively.

The results of these studies are shown in Figure 2.3. Let us note that the amounts of cement bound water in this case are higher than in chemical analysis due to the fact that the samples were not pre-desiccated at  $105^{\circ}\text{C}$ . Chemical and differential thermal analyses show that the interaction of cement with water begins immediately after mixing it.

With further hydration of the cement the amount of strongly bound water increases and upon chemical analysis of the Belgorod cement is 0.17% 15 minutes after mixing; 0.47% 6 hours, 1% 12 hours and 3.01% 1 day.

The strongly bound water contained in cement powder before mixing is excluded from these determinations.

The hydration process proceeds more rapidly during the first hours in Voskresenskiy cement than in Belgorod cement. The increase in cement hydration in freezing weather can be explained by the additional binding

of water by highly dispersed calcium hydrosilicates formed at reduced temperatures during freezing and thawing. After curing at a temperature of  $-2^{\circ}\text{C}$  for 28 days the binding of the water reached 10 and 11.4% for Belgorod and Voskresenskiy cements (curve 2), and at  $-5^{\circ}\text{C}$  it dropped to 5.7% (curve 3). But the endothermic effect of the decomposition of  $\text{Ca}(\text{OH})_2$  is completely missing on the thermograms of samples frozen immediately after manufacture at  $-10$  or  $-20^{\circ}\text{C}$  (Figure 2.3, curves 4 and 5 for both cements). The latter indicates that the hydration reactions have stopped at these temperatures.

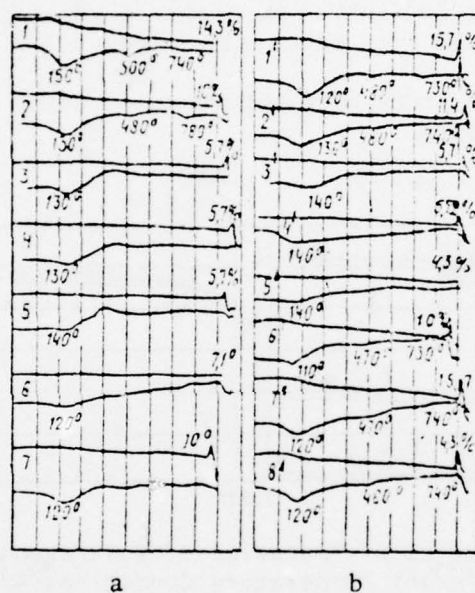


Figure 2.3. Sample Thermograms. a, Made using Belgorod cement: 1, 28 days of normal hardening; 2, Frozen immediately at  $t = -2^{\circ}\text{C}$  and cured 28 days in freezing weather; 3, The same at  $t = -5^{\circ}\text{C}$ ; 4, Frozen immediately at  $t = -10^{\circ}\text{C}$  and cured 28 days in freezing weather; 5, The same at  $t = -20^{\circ}\text{C}$ ; 6, 12 hours of normal storage; 7, Frozen 12 hours at  $t = -20^{\circ}\text{C}$  and cured 28 days in freezing weather; b, Made using Voskresenskiy cement: 1', 28 days of normal hardening; 2', Frozen immediately at  $t = -2^{\circ}\text{C}$  and cured 28 days in freezing weather; 3', The same at  $t = -5^{\circ}\text{C}$ ; 4', The same at  $t = -10^{\circ}\text{C}$ ; 5', The same at  $t = -20^{\circ}\text{C}$ ; 6', 24 hours of normal hardening; 7', Frozen 24 hours at  $t = -5^{\circ}\text{C}$  and cured 28 days in freezing weather; 8', The same at  $t = -20^{\circ}\text{C}$ .

Two additional experiments were conducted to better understand the certain difference concerning the degree of hydration between the cement samples frozen soon after manufacture and then hardened 28 days under normal conditions and the samples hardened all 28 days under normal conditions. In the first series samples were manufactured from the minerals of cement clinker  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  and from two high aluminate clinkers of portland cements from the Spasskiy and Nikolayevskiy Factories.



The samples were frozen immediately after manufacture at  $-5^{\circ}\text{C}$ , cured at this temperature 7 days, then 28 days under normal conditions. Some of the samples of these minerals and clinkers were stored under normal conditions. As the test results given in Table 2.9 have shown, the degree of hydration of frozen samples of  $\text{C}_3\text{A}$  differs hardly at all from standard samples, and that of clinkers from the Nikolaveyskiy and Spasskiy Factories differs insignificantly (in all 1-2% according to data of x-ray analysis). The degree of hydration of samples of  $\text{C}_3\text{S}$  drops 8% compared with standard samples. Thus, we can say that freezing exerts almost no effect on subsequent hydration of  $\text{C}_3\text{A}$  and clinkers with a high content of  $\text{C}_3\text{A}$ .

Samples were prepared using Belgorod cement for the second series of tests. Some of them were hardened 28 days in an exsiccator at  $20^{\circ}\text{C}$  over water and in water, the others were frozen immediately after manufacture at  $-20^{\circ}\text{C}$  and cured at this temperature for 7 days and then hardened also in an exsiccator at  $20^{\circ}\text{C}$  over water and in water. Upon comparison of the data of these studies it was found that samples hardened at an above zero temperature in water have a somewhat higher degree of hydration than samples cured 28 days over water; the degree of hydration of samples hardened after thawing in an exsiccator over water is less than that of those hardened the entire time in an exsiccator under water, and in samples cured after thawing in water it is somewhat higher than in samples cured in water at  $20^{\circ}\text{C}$ .

We may conclude from what has been stated above that freezing has a positive effect on the degree of hydration of samples after thawing in view of the superior dissolution of lime and the greater permeability of the envelopes around the cement grain at reduced temperatures. However, subsequent sample storage conditions have a great effect on the degree of hydration since due to the considerable loss of moisture in freezing weather, and especially during thawing and subsequent hardening even in a normal storage chamber, the degree of hydration of samples may subsequently drop dramatically (which was established in the initial experiments), especially in samples of cements with a low content of aluminate components. A drop in the degree of hydration was not observed or it was very insignificant in samples with a greater content of aluminate components. This fact is apparently explained by the more rapid course of the interaction processes of the aluminate components with water as well as by their ability to easily give up water to the surrounding medium when its humidity is reduced.

The following conclusions can be drawn on the basis of the research conducted.

The interaction of cement with water begins immediately after it is mixed; this is indicated by the presence of strongly bound water which is determined by chemical analysis. Subsequently the amount of this water gradually increases during the entire period.

TABLE 2.9. EFFECT OF FREEZING ON THE SUBSEQUENT DEGREE OF HYDRATION  
OF MINERALS  $C_3S$ ,  $C_3A$  AND CLINKERS FROM THE  
NIKOLAVEYSKIY AND SPASSKIY FACTORIES

Hardening Conditions	Degree of hydration in terms of the amount of hydrated $C_3S$ , %	Amount of strongly bound water according to data of chemical analysis, %* (L.o.c.** 1000)
Degree of hydration of $C_3S$ for 28 days of normal storage	62.5	11.55
The same, frozen immediately after manufacture at $-5^{\circ}C$ and stored 7 days in freezing weather and 28 days under normal conditions	54.2	9.62
Degree of hydration of $C_3A$ for 28 days of normal storage	67.5	25.5
The same, frozen immediately after manufacture at $-5^{\circ}C$ and stored 7 days in freezing weather and 28 days under normal conditions	67	25.4
Samples of Nikolaveyskiy clinker for 28 days of normal storage	81	13.82
The same, frozen immediately after manufacture at $-5^{\circ}C$ and stored 7 days in freezing weather and 28 days under normal conditions	79.8	13.3
Samples of Spasskiy clinker for 28 days of normal storage	85.5	16.08
The same, frozen immediately after manufacture at $-5^{\circ}C$ and stored 7 days in freezing weather and 28 days under normal conditions	83.4	15.19

\*Without considering the water contained in the mineral  
or clinker before mixing.

\*\*Loss on calcination.

Especially intensive development of the processes of cement hydration is observed after 12 hours of normal hardening. Qualitative x-ray analysis also shows that a noticeable increase in calcium hydroxides occurs in the new formations from this age.

The greatest binding of water by cement occurs by three days of normal storage, when the amount of strongly bound water and the amount of hydrated  $C_3S$  is approximately 70-80% of these values at age 28 days.

Cement hydration and heat liberation, and consequently concrete hardening, although quite slow, continue at high sub-zero temperatures. Hydration and heat liberation (and also strengthening) practically cease in cement paste (and concrete) frozen immediately and also 3, 6, 9 hours after manufacture at a temperature below  $-10^{\circ}\text{C}$ .

A test was conducted with samples of Belgorod cement to check the effect of humidity conditions when determining the true values which characterize the degree of hydration. In this case the samples were in an exsiccator at  $t = 20^{\circ}\text{C}$  above water or in water. Some of them were frozen at  $t = -20^{\circ}\text{C}$  for 7 days and then hardened for 28 days at normal temperature. The second part of this same series of samples was in water or over water at normal temperature for 28 days in all.

The results of quantitative x-ray analysis are shown in Figure 2.4. As can be seen from the data shown in the diagram, the degree of hydration of cements frozen at an early age subsequently during hardening under above zero temperature and adequate humidity conditions does not significantly differ from the degree of hydration of cements cured for the entire period at an above zero temperature.

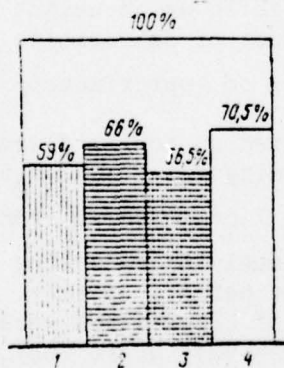


Figure 2.4. Diagram of the Degree of Hydration of Samples Hardened 28 Days in an Exsiccator. 1, 2, Above water and in water at  $t = 20^{\circ}\text{C}$  respectively; 3, 4, The same after 7 days of freezing at  $t = -20^{\circ}\text{C}$ .



Experience has shown that the degree of cement hydration may drop as the result of the loss of part of the capillary water during the hardening of samples, after exposure to freezing weather, or in a facility or chamber with insufficient humidity which occurred in the experiment described earlier (see Figure 2.2). It was ascertained that the degree of hydration increases in water when curing similar samples after exposure to freezing weather.

In this case the lag in the degree of hydration of frozen samples during subsequent curing under ordinary air-humidity conditions is not observed in high aluminates cements or it is very insignificant.

It has been concluded on the basis of the results of qualitative x-ray analysis that the phase composition of new formations in samples which have been frozen does not differ from test samples of them hardened for the entire period under normal conditions. Consequently from the point of view of chemical analysis, freezing affects only the kinetics of hydration, and not the quantitative aspect of the processes.

The results of studies cited previously about the effect of sub-zero temperatures on cement hydration were obtained in the laboratory as a result of the development of the candidate dissertation of L. A. Belova [3] during 1970-1973.

We will only cite data from earlier works on this problem which were obtained in elaborating the topic of hardening of light concretes under different temperature-humidity conditions. Cement hydration was studied in terms of the amount of chemically bound water by measuring loss in calcining samples at  $600^{\circ}\text{C}$  and also in terms of the amount of free CaO determined using the ethylene glycol method. In addition, differential thermal analysis was conducted in which weight losses were determined within the limits of the effect of dehydration of  $\text{Ca}(\text{OH})_2$  and the total loss of mass at a temperature of approximately  $1000^{\circ}\text{C}$  [34].

The studies were conducted on portland cement from the Novo Zdobunovskiy Factory containing  $\text{C}_3\text{S}$  - 60%;  $\text{C}_2\text{S}$  - 18%;  $\text{C}_3\text{A}$  - 8%;  $\text{C}_4\text{AF}$  - 13%. Samples  $7 \times 7 \times 7$  cm prepared from cement paste with a  $\text{W/C} = 0.3$  were placed immediately in a cooling chamber with temperatures of  $-5$  and  $-20^{\circ}\text{C}$  for different periods of time. After 7 days of exposure to freezing conditions some of the samples were transferred to a normal storage chamber ( $t = 20^{\circ}\text{C}$ ,  $\text{W} = 90\%$ ) where they were hardened for 28 and 60 days more. At the same time control samples were prepared which were placed in a normal storage chamber for 28 and 60 days. The samples were dehydrated with alcohol, rubbed with filter paper and ground into a fine powder.

The samples were dried at  $100^{\circ}\text{C}$  for chemical analysis. Losses on calcination, free CaO and  $\text{CO}_2$  were determined in a prepared sample by directly weighing it. The results of these analyses are shown in Table 2.10. It follows from the data obtained that the content of

chemically bound water at sub-zero temperatures, especially at  $-20^{\circ}\text{C}$ , is comparatively great. This is apparently due to the fact that water is included here which is chemically bound by cement powder and partially hydrated before mixing the cement paste. At the same time it may be noted that high alite, aluminate finely ground cement was used.

Studies of cement hydration and concrete strengthening at sub-zero temperatures are associated with the cooling and thawing of samples. In this period it is methodologically difficult to exactly consider the value of the processes occurring. After the samples remain in the chamber at  $t = -5^{\circ}\text{C}$  considerably more chemically bound water and free  $\text{CaO}$  were obtained than at  $-20^{\circ}\text{C}$ . This indicates a positive course of cement hydration processes at such a temperature as  $-5^{\circ}\text{C}$ .

TABLE 2.10. EFFECT OF SUB-ZERO TEMPERATURES  
ON CEMENT HYDRATION

Hardening Conditions	Chemically bound water (loss on calcination at $600^{\circ}\text{C}$ )	$\text{CaO}_{\text{free}}$	$\text{CO}_2$	Total theoretical $\text{CaO}$
7 days in a normal storage chamber	10.11	6.85	3.5	9.6
28 days in a normal storage chamber	11.5	7.1	4.6	10.71
60 days in a normal storage chamber	15	7.5	5	11.42
28 days under refrigeration at $t = -5^{\circ}\text{C}$	3.78	2.38	3.09	4.9
28 days under refrigeration at $t = -20^{\circ}\text{C}$	2.31	0.75	2.47	2.69
7 days at $t = -5^{\circ}\text{C}$ followed by 28 days under normal conditions	9.84	5.84	5.82	10.41
7 days at $t = -20^{\circ}\text{C}$ followed by 28 days under normal conditions	9.12	2.2	8.89	9.17
7 days at $t = -5^{\circ}\text{C}$ followed by 60 days under normal conditions	15.12	4.79	7.52	10.69
7 days at $t = -20^{\circ}\text{C}$ followed by 60 days under normal conditions	15.29	3.46	8.33	10

The data of mass loss within the limits of  $\text{Ca(OH)}_2$  dehydration agree with the results obtained in differential thermal analysis. Some difference is due to the fact that in preparing the samples for chemical analysis, they were dried at  $100^\circ\text{C}$  after dehydration with alcohol, and this was not done in the differential thermal analysis. The results of studies of cement hydration are shown in Table 2.11 according to the data of differential thermal analysis.

TABLE 2.11. EFFECT OF SUB-ZERO TEMPERATURES ON CEMENT HYDRATION ACCORDING TO THE DATA OF DIFFERENTIAL THERMAL ANALYSIS

Hardening Conditions	Adsorption and hydrate water	Water in $\text{Ca(OH)}_2$	Losses on calcination at $600^\circ\text{C}$	$\text{CaCO}_3$	Total mass losses at $1000^\circ\text{C}$
28 days in a normal storage chamber	6	4	10	4	14
60 days in a normal storage chamber	8.5	6.5	15	5	20
28 days under refrigeration at $t = -5^\circ\text{C}$	2	1.5	3.5	3.5	7
28 days under refrigeration at $t = -20^\circ\text{C}$	1	1	2	1	3
7 days at $t = -5^\circ\text{C}$ , followed by 28 days under normal conditions	9	2	11	7	18
7 days at $t = -20^\circ\text{C}$ , followed by 28 days under normal conditions	6	4	10	10	20
7 days at $t = -5^\circ\text{C}$ , then 60 days under normal conditions	9	6	15	5	20
7 days at $t = -20^\circ\text{C}$ , then 60 days under normal conditions	10	5	15	6	21



It can be seen from the table that, just as from the data of chemical analysis, more considerable hydration of samples is observed at  $-5^{\circ}\text{C}$  than at  $-20^{\circ}\text{C}$ . At sub-zero temperatures the carbonization of  $\text{CaO}$  increases due to the absorption of carbon dioxide from the air.

After freezing concrete at an early age and subsequently hardening it at above zero temperatures, cements maintain the ability to chemically bind as much and even (in some cases) more water than in samples which have not been frozen.

However, as will be shown later, in spite of the hydration processes which subsequently take place in the presence of new formations, concrete usually loses strength after early freezing compared to normal hardening. This is associated with the formation conditions of the structure of the cement stone in concrete when it is frozen at an early age. Therefore the kinetics and degree of hydration of cement cannot be considered unrelated to the structure formation conditions, or to the degree of solidity of the cement stone in concrete.

The rate and degree of cement hydration can be increased by introducing chemical additives which lower the freezing point of the liquid phase. Table 2.12 presents data on the degree of hydration of cement tricalcium silicate with an admixture of sodium nitrite and potash which were obtained by I. I. Komarov, Yu. M. Butt and V. N. Kolbasov at the D. I. Mendeleyev Moscow Industrial-Technology Institute.

TABLE 2.12. DEGREE OF CEMENT HYDRATION  
AT DIFFERENT TEMPERATURES FOR 28 DAYS  
(PASTE 1:0, WITH W/C = 0.25)

Additive		Degree of hydration, %, at a temp., $^{\circ}\text{C}$			
Type	Amount in % of cement mass	20	0	-10	-20
Without additive	—	66	39	20	1
$\text{NaNO}_2$	2	64	44	43	17
	10	67	43	42	27
$\text{K}_2\text{CO}_3$	10	55	41	46	37

The samples were studied using quantitative x-ray analysis. The portland cement used was composed of:  $\text{C}_3\text{S}$  - 64.43%;  $\text{C}_2\text{S}$  - 15.8%;  $\text{C}_3\text{A}$  - 6.04%;  $\text{C}_4\text{AF}$  - 9.82% with a grinding fineness of  $3150 \text{ cm}^2/\text{g}$ . The degree of cement hydration was ascertained from tricalcium silicate. At  $20^{\circ}\text{C}$  a 10% addition of potash retards cement hydration, at  $0^{\circ}$  it proceeds at the same rate as in cements without the additive and with the sodium nitrite additive. At  $-10$  and  $-20^{\circ}\text{C}$  cement hydration proceeds with maximum speed when potash is added. Even in quantities as small as 2% the addition of sodium nitrite ensures quite intense cement hydration.

The degree and rate of cement hydration at sub-zero temperatures with chemical additives depend on the temperature, amount and type of additives introduced, the mineralogical content and fineness of the grinding of the cement and other factors.

In spite of the successes achieved in recent years in studying the mechanism of the action of chemical additives on the properties of concrete mixtures and concrete, many of the questions of this problem have still not been adequately treated. Research being carried out by scientists in the USSR as well as abroad on the use of chemical additives in winter concreting should be expanded.

#### Cement Heat Liberation at Different Temperatures.

The hydration reaction of clinker minerals and cement as the result of which they set and harden is accompanied by the liberation of heat. A definite relationship between mineralogical content, hydration, liberation of heat and hardening of cements has been experimentally established.

The processes of heat liberation depend on the properties of the cement, its content in the concrete, time, temperature, the water-cement ratio and other factors. Since it is the direct result of cement hydration, the liberation of heat characterizes the development of hardening processes of concretes and mortars and determines their technical properties, all other conditions being equal. It may exert a positive as well as a negative influence on the formation of the structure and technical properties of concretes and mortars. Even in winter concreting of massive structures the question often arises of controlling the heat liberation process in order to avoid a damaging thermally stressed state of the structures. The "thermos" method which was developed and is widely used in our country during winter concreting and reinforced concreting operations is based to a considerable degree on calculating heat liberation in hardening concrete in thermotechnical computations.

Cement heat liberation was studied as far back as more than 50 years ago and is presently being studied in many countries. In the USSR these studies were mainly associated with hydrotechnical construction. The works of the following authors, beginning in the twenties, are well-known: A. A. Baykov, V. A. Kind, S. D. Okorokov, L. S. Volfson, V. N. Yung, Yu. M. Butt, V. S. Lukyanov [29].

In 1919, I. A. Kireyenko attempted to calculate concrete cooling in freezing weather with consideration of cement heat liberation [22]. In 1935, the author compared new methods of calculating concrete cooling in freezing weather with consideration of heat liberation which were proposed by I. A. Kireyenko, B. T. Skrantayev, V. S. Lukyanov et al. on an experimental basis.

Recently the Leningrad Polytechnic Institute has been conducting work to determine a heat liberation of cement in concrete. The results of these studies are summarized in the monograph of I. D. Zaporozhets,

S. D. Okorokov and A. A. Pariyskiy [17]. This institute conducted research of interest to builders on heat liberation when electrically heating concrete to 70°C, under normal, zero and sub-zero (down to -10°C) conditions. This work was conducted together with the Scientific Research Institute of Concrete and Reinforced Concrete. Concurrent with research on heat liberation of cements in concrete the Scientific Research Institute of Concrete and Reinforced Concrete conducted research on studying cement hydration and on concrete hardening under the same above-zero and sub-zero temperatures.

Among the works of foreign authors in the field of determining the kinetics of heat liberated by cements of varying mineralogical content with simultaneous determination of their strengthening, the studies of V. Lerch and R. Bogg in the U.S.A. which were published at the beginning of the thirties should be mentioned first of all. They were the first to study heat liberation of not only cements of a specific composition, but of all the basic minerals making up portland cement clinker. In 1929 H. Davis and O. Troksell studied questions of heat liberation in concrete blocks. In the 1940's interesting studies were made by G. Verbek and S. Foster in the U.S.A. in the field of cement heat liberation.

On the basis of work conducted in the FRG, A. Mayer proposed a classification of cements according to the amount of heat liberated. These data were presented in the recommendations of the RILEM on winter concreting published in Russian, English, French and German. A more practical classification of cements according to the kinetics and amount of heat liberated in hardening of concretes containing cements of various types and grades has been developed in the USSR. In France, M. Venua has conducted broad studies on heat liberation of portland cement with various additives. This research was carried out within the framework of Franco-Soviet scientific technical cooperation from 1969 through 1972.

After correlating the studies carried out scientists concluded that, as any chemical reaction, cement hydration begins with a physical phenomenon - the dissolution of the minerals. Heat liberation is the result of this chemical reaction. The chemical reaction of hydration is the cause, and heat liberation is the result of it taking place.

A contradiction is hidden in the fact of heat liberation in concrete; it is expressed in that the warming-up of a structure may be useful to create favorable hardening conditions and at the same time it may cause a stressed state and the destruction of its structural integrity. In winter, medium-size structures may be cured using the thermos method; but very massive structures may acquire surface cracks which reduce their lifetime not only at above zero, but also at sub-zero outside air temperatures unless special measures are taken. In order to use heat liberation in a directed manner in all cases, we must know the exact calculation of thermal fields in concrete and reinforced concrete structures and ensure uniformity of their distribution. However, there are great difficulties in solving this problem which are associated with the diverse conditions of heat and moisture distribution within the concrete, with the considerable



gradients of them, and with the frequently varied direction of movement of heat and moisture.

Theoretical calculations are considerably complicated as the result of the time changes in the physical constants of concrete and the irregularity of the flows and thermal mass transfer with any outside medium. Many questions are still subject to experimental study in accordance with well-founded scientific procedures, with a thorough understanding of the application of thermodynamic laws. In this area more than in any other, the method of dialectic examination of a complex set of phenomena should be used and mechanical methods of calculation isolated from the physical essence of the occurring processes must not be allowed. Calculations for building practice should be as simple and clear as possible; only then will they be widely used.

Notwithstanding the method of prehydration of cement proposed in the U.S.A. by P. Bates in 1937, the author has suggested and developed a new method described in the book "The Temperature Factor in the Hardening of Concrete". Instead of prehydrating cement by treating it with steam in a drum and subsequently using it in massive structures after predrying and grinding (Bates' method), the author has suggested that some of the heat liberated by the cement be damped by treating it in special hydrators. Mixing the cement suspension with cold water and prolonged curing of it while mixing it in the hydrators reduces heat liberation, but not due to a reduction in the activity of the cement, and conversely, at the same time increases the activity of the cement and resistance of the concrete, especially to rupture.

The author together with S. F. Bugrim and Ye. S. Stanislavova have suggested a method of placing concrete in contact with permafrost soil using heat liberation [66]. In this case the heat of cement hydration and the heat liberated during the phase transition of water from a liquid to a solid is used to harden the concrete at frozen ground temperatures of from  $-0.2$  to  $-2^{\circ}\text{C}$ . At lower temperatures small quantities of antifreeze agents must be added.

The first standards for heat liberation by different cements at normal temperature for 28 days were set forth in the Technical Specifications for Winter Reinforced Concrete Operations in the early 1930's. During the past forty years the quality of cements has improved, the grades of concretes used have risen and experimental data has been accumulated on the heat liberation of cements at different temperatures. Therefore new practical data for cements are cited below which must be known when choosing winter concreting methods and thermal treatment conditions.

S. D. Okorokov conducted broad studies on determining heat liberation by individual minerals and by mineral mixtures. Heat liberation was determined from the difference of dissolution heats in non-hydrated and hydrated states. The results obtained by him are shown in Table 2.13.

TABLE 2.13. HEAT OF HARDENING OF PORTLAND CEMENT  
MINERALS AND THEIR MIXTURES

Mineralogical content				Heat liberation, kJ/kg					
C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>4</sub> AF	Actual			Theoretical		
				3 days	28 days	3 months	3 days	28 days	3 months
Mixtures of C <sub>3</sub> S and C <sub>2</sub> S									
100	—	—	—	322.4	389.4	456.4	—	—	—
75	25	—	—	217.7	255.4	355.9	247	318.2	381
50	50	—	—	171.7	209.4	305.7	175.9	251.2	305.7
25	75	—	—	129.8	175.9	217.7	100.5	180	226.1
—	100	—	—	25.1	108.9	150.7	—	—	—
Mixtures of C <sub>3</sub> S and C <sub>3</sub> A									
100	—	—	—	322.4	389.4	456.4	—	—	—
95	—	5	—	334.9	418.7	477.3	330.8	410.3	477.3
85	—	15	—	452.2	540	548.5	347.5	448	515
75	—	25	—	456.4	577.8	607.1	368.5	485.7	552.7
—	—	100	—	502.4	778.7	833.2	—	—	—
Mixtures of C <sub>3</sub> S and C <sub>4</sub> AF									
100	—	—	—	322.4	389.4	456.4	—	—	—
95	—	—	5	247	376.8	410.3	314	389.4	452.2
85	—	—	15	238.7	343.3	401.9	293.1	385.2	448
75	—	—	25	200.9	309.8	381	276.3	381	433.8
—	—	—	100	133.9	364.3	397.8	—	—	—

Commas indicate decimal points

In addition to actual heat liberation established experimentally, this table gives theoretical heat liberation as well which is calculated for mineral mixtures in accordance with the additivity principle.

Table 2.13 shows that upon hydration C<sub>3</sub>A and C<sub>2</sub>S differ not only in high, but in rapid heat liberation. C<sub>4</sub>AF and especially C<sub>2</sub>S are slightly thermal and liberate heat considerably more slowly. Hence it follows that to obtain low-heat portland cements it is necessary to reduce their content of C<sub>3</sub>A and C<sub>2</sub>S by increasing the content of C<sub>3</sub>S in the aluminoferrite phase. And conversely, to obtain cements with high heat liberation it is necessary to increase the content of tricalcium aluminate and tricalcium silicate.

S. V. Sharkunov and A. S. Magiton of the S. Ye. Zhuk All Union Planning, Surveying and Scientific Research Institute experimentally studied the problem of heat liberation of concrete under adiabatic conditions of 10 different cements. These cements were taken from the Toktogulsk, Ingursk, Nureksk, Ust-Ilinsk hydraulic projects and from buildings under construction in Syria, Vietnam, Tunisia, Afghanistan. Figure 2.5 shows the curves of specific heat liberation of certain types of cements in concrete of industrial compositions for 14 days, and Table 2.14 gives the characteristics of the concretes mixed from these cements. In the 14 day period the cements liberated heat of from 250 to 335 kJ/kg. During the first 3 days the relative liberation of heat differed considerably in concretes containing various cements.

TABLE 2.14. CHARACTERISTICS OF CONCRETES CONTAINING  
VARIOUS CEMENTS (ACCOMPANYING FIGURE 2.5)

Number of the Curve	Cement	Concrete characteristics		
		Cement consumption, kg	W/C	Mixture Temperature, °C
1	Portland cement M 300, Krasnoyarsk Factory	180	0.75	14
2	The same, Dushanbinsk Factory	185	0.75	25
3	The same, Kuvasaysk Factory	210	0.60	15
4	The same, "Sheikh-Said" (Syria, "Tabka", Hydroelectric Station)	240	0.55	22
5	The same, with a reduced content of $C_3S$	225	0.65	17
6	The same, Pozzuolanic cement, Kuvasaysk Factory	215	0.56	17
7	The same, Rustavsk Factory	270	0.43	16
8	The same, "Poli-Khumri" (Afghanistan, Hydroelectric Station)	180	0.85	17
9	The Same, Nagli Karruba (Tunisia)	270	0.5	20.5
10	Grade 200 slag portland cement, Krasnoyarsk Factory	210	0.65	10

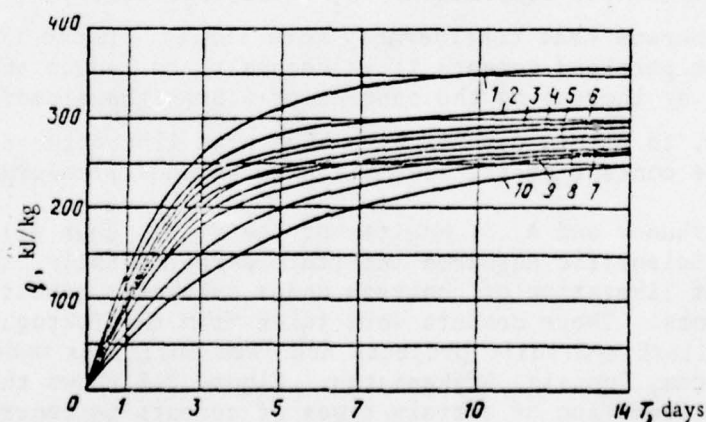


Figure 2.5. Curves of Specific Heat Liberation of Cements  
(As Per GOST 310-60) Determined in an Adiabatic Calorimeter  
on Samples of Concrete of Various Industrial Compositions  
(Curve Designations Shown in Table 2.14).



As is apparent from the list of cements, from 180 to 270 kg of each was consumed per cubic meter; this is characteristic of hydrotechnical concretes.

The dependency of cement heat liberation on temperature has been studied at the All Union Scientific Research and Planning Institute for Heat Engineering Structures. Members of this Institute I. B. Zasedatelev and F. M. Mamedov developed a method of experimentally determining heat liberation in an electrical differential calorimeter. Different temperatures and pressures are created in an autoclave using compressed gas; this ensured the possibility of separately examining these two factors. The kinetics of heat liberation  $q$  were studied in the 20 to 174°C temperature range. The results of studies of portland cement with the following composition:  $C_3S$  - 64%;  $C_2S$  - 14%;  $C_3A$  - 4%, are shown in Figure 2.6.

A cement mixture with ground sand was made with a  $W/C = 0.8$ .

Experiments have shown that pressure exerts little influence on the liberation of heat; the temperature at which cement hydration takes place is the decisive factor.

A. A. Pariiskiy of the Leningrad Polytechnic Institute built a device and developed a procedure for experimentally determining isothermic heat liberation of cement mortars and concretes. In doing this two basic conditions should be ensured throughout the experiment: constancy of the temperatures of the hardening concrete and calorimetric envelope. The amount of electrical energy consumed to maintain the concrete temperature at the set level is automatically monitored by the device. Table 2.15 shows the results of these studies which were conducted in cooperation with the Scientific Research Institute of Concrete and Reinforced Concrete. It shows data on heat liberation on three typical cements at temperatures: 0; 20; 40; 50 and 70°C. The test was conducted for 10 days, and for slag portland cement concrete approximately 14 days. The concrete mixture had a slump of 6-8 cm at a cement consumption of 325 kg/m<sup>3</sup>. Tests showed that at 0°C heat liberation proceeds quite intensely: it was 59% of heat liberation at  $t = 20^\circ\text{C}$  in portland cement for 10 days. Data on heat liberation in the 40-70°C temperature range are cited first. They may be fully utilized in thermal treatment of concretes. No less interesting are the data on determining heat liberation by grade 500 portland cement and grade 600 quick hardening portland cement in concrete at  $W/C = 0.52$ . Chloride salts, potash and sodium nitrate were added to the concrete in amounts of 10% of the water mass. Retardation of the rate of heat liberation at  $t = -10^\circ\text{C}$  is especially great the first 3 days. Even at age 10 days it is several times smaller than heat liberation at 0°C without additives.

The heat liberation in grade 500 portland cement with a grinding fineness of 3150 cm<sup>2</sup>/g with added chloride salts and sodium nitrite is considerably less than in grade 600 cement. The same cement ground to a fineness of 5000 cm<sup>2</sup>/g increased its activeness by one grade, i.e., became grade 600 quick-hardening cement. However, its rate of heat liberation with additives increased considerably compared to the initial grade 500 cement. The results of these determinations for concrete with cement consumption 325 kg/m<sup>3</sup>,  $W/C = 0.52$ , slump = 6-8 cm are shown in Table 2.16.

TABLE 2.15. SPECIFIC HEAT LIBERATION OF PORTLAND CEMENT, QUICK HARDENING CEMENT AND SLAG PORTLAND CEMENT AT DIFFERENT TEMPERATURES OF ISOTHERMIC CONCRETE HARDENING

Cement	W/C	t, °C	Specific heat liberation of cements, kJ/kg, at age, hours														
			6	12	18	24	36	48	72	96	120	144	168	192	216	258	336
Portland cement Grade: 500 300	0.52	0	—	—	—	18	32.7	52.8	88.8	111.7	132.3	148.6	161.2	171.2	187.9	—	—
		20	—	37.7	—	111.4	159.9	185.9	220.2	245.1	272.9	277.2	290.2	299.8	316.5	—	—
		40	—	—	146.8	231.1	251.2	274.2	301.5	319.9	329.1	—	—	—	—	—	—
		70	—	—	—	157.6	—	229	241.9	257.9	251.7	262.1	261.6	—	—	—	—
Grade 600 quick hardening cement	0.52	0	—	—	—	27.6	52.8	73.7	101.3	131.1	151.9	168.3	180	191.8	201.4	—	—
		20	—	58.6	—	117.3	150.5	212.7	272.9	290.2	310.7	325.1	335.1	345.4	352.1	—	—
		40	103.3	191.7	237.8	265.9	299.1	320.7	343.8	358.8	367.5	—	—	—	—	—	—
		70	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Grade 300 slag portland cement	0.6	5	—	—	—	21.1	—	53.2	79.9	99.7	113	123.9	133.6	141.9	148.6	166.2	171.2
		10	—	—	—	40.6	—	71.9	99.7	117.2	128.9	141.5	151.6	159.5	166.2	183.3	—
		20	—	—	—	71.5	—	121.1	133.7	167.9	170	170.1	197.6	201.3	210.6	222.3	230.7
		50	—	—	—	167.1	—	193.4	211.1	220.2	228.6	234.9	241.6	—	—	—	—
		70	—	—	—	203.1	—	233.2	245.4	252.5	251.2	255.4	256.2	—	—	—	—

Note. At a temperature of -10°C no heat liberation was observed in concrete without antifreeze additives. Commas indicate decimal points.

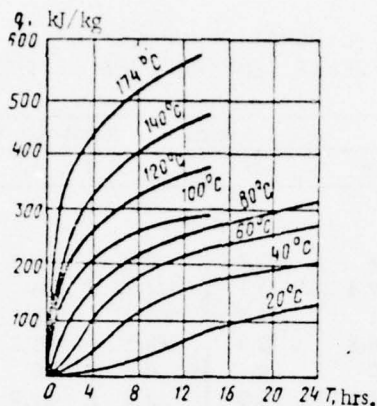


Figure 2.6. Hydration Heat as a Time Function of Temperature.

Along with data on portland cement concrete, an examination of data on slag portland cement concrete and ozzuolanic portland cement concrete is of interest. In many countries (U.S.A., France, Japan and others) cement additives of not only granular furnace slag but also ashes from power plants are widely used.

Manufacture of slag portland cements using granular furnace slags has been known in German industry since 1863. Later furnace slag began to be widely used as a raw material for producing portland cement.

At present considerable amounts of slag portland cement are produced in the USSR, the FRG, Belgium, Italy, France, Japan and other countries.

In spite of the retarded liberation of heat by slag portland cement in initial periods, almost as much heat is evolved when the cement is fully hydrated, i.e., after a prolonged time interval, as by cement without added slag.

With consideration of its heat liberation and resistivity in aggressive media, slag portland cement is widely used in foreign as well as Soviet hydrotechnical construction and when erecting massive structures. Slag portland cement concrete has already been used in restoring the Dnepr hydroelectric station and in building the Kakhovsk hydroelectric station.

Active mineral additives (tripoli, waste ashes and others) are even more widely used to reduce heat liberation and increase the water resistance of concrete in Soviet and foreign hydrotechnical construction practice.

The effect of adding Bryansk tripoli and quartz sand on the specific heat liberation of cements using clinker from the Vorovskiy Leningrad Cement Factory has been studied at the Leningrad Polytechnic Institute. The concretes were mixed using the same amount of cement,  $250 \text{ kg/m}^3$ , with the same consistency of the mixture. The latter caused a varying water requirement, and consequently affected the water-cement ratio. The results of tests under isothermic conditions  $t = 20^\circ\text{C}$  are shown in Table 2.17.



TABLE 2.16. SPECIFIC HEAT LIBERATION OF CEMENT IN CONCRETES WITH ANTIFREEZE ADDITIVES AT DIFFERENT TEMPERATURES OF ISOTHERMIC HARDENING

Temp. °C	Additives		Specific heat liberation, kJ/kg at age, hours						
	Type	%	21	43	72	120	168	192	210
Portland cement									
0	Without additives	0	18	52,8	88,8	132,3	161,2	171,2	187
	CaCl <sub>2</sub> +NaCl	3+7	39,8	78,7	111,8	169	207,7	221,9	245,8
	K <sub>2</sub> CO <sub>3</sub>	10	54	104,7	159,1	225,7	257,5	269,2	288,5
	NaNO <sub>2</sub>	10	36,8	72,4	100,5	150,3	193,9	212,7	244,9
-10	Without additives	0	0	0	0	0	0	0	0
	CaCl <sub>2</sub> +NaCl	3+7	2,5	6,3	9,6	22,6	33,1	36	45,2
	K <sub>2</sub> CO <sub>3</sub>	10	5	12,9	21,8	53,2	82,1	96,3	118,5
	NaNO <sub>2</sub>	10	0	0	0,8	7,5	15,5	20,9	29,3
20	Without additives	0	111,4	185,9	220,2	262,9	289,7	299,8	316,5
Quick hardening cement									
-10	Without additives	0	0	0	0	0	0	0	0
	CaCl <sub>2</sub> +NaCl	3+7	10,5	20,9	22,6	60,3	82,5	90,9	108,4
	K <sub>2</sub> CO <sub>3</sub>	10	10,9	23,7	40,6	78,7	112,2	126,4	145,7
	NaNO <sub>2</sub>	10	0	0	5,9	36,8	68,7	82,1	105,9
20	Without additives	0	137,3	212,7	257,9	310,7	335,8	345,4	357,2

Note. Added NaNO<sub>2</sub> and K<sub>2</sub>CO<sub>3</sub> are given in % of the cement mass, CaCl<sub>2</sub> and NaCl in % of water mass. Commas indicate decimal points.

These data which confirm the assertions of many researchers show that the introduction of up to 25% active hydraulic additives leads to a small drop in heat liberation. In this case the grinding fineness of the cement and the activity of the components are important.

The addition of furnace slags to portland cement clinker is more effective than other mineral substances, including active ones, for purposes of saving cement and in terms of a number of the engineering properties of concrete.

Full-scale studies on heating cement in dam blocks were conducted by the Siberian Branch of the B. E. Vedeneyev All Union Scientific Research Institute of Hydraulic Engineering when erecting the concrete structures of the Krasnoyarsk hydroelectric station. The results of temperature measurements in the center of concrete blocks poured in winter, 1962, are shown in Figure 2.7. After 24 days of hardening the maximum temperature rise in the blocks was 31-38°C, and the minimum 16°C, compared to the temperature during placement. The principal characteristics of the blocks, the cements used, etc., are shown in Table 2.18.

TABLE 2.17. THE ADDITIVE EFFECT ON CEMENT HEAT LIBERATION

Additives	Additive content, %	W/C	Heat liberation, kJ/g, at age, days							Reduction in heat liberation for 7 days, %
			2	3	4	5	6	7	8	
Without additive	0	0,75	170,8	222,7	259,6	289,7	316,5	336,6	353,4	0
Bryansk	25	0,79	164,1	200,9	232,8	259,6	284,7	306,5	324,9	9
Tnpoli	50	0,89	117,2	144	164,1	180,9	194,3	206	216	39
Quartz	25	0,75	128,9	169,2	197,6	221,1	242,8	261,2	278	22
Sand	50	0,75	107,2	135,7	154,1	170,8	181,2	193,95	213,5	42

Commas indicate decimal points.

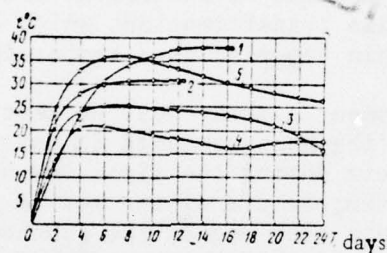


Figure 2.7. Concrete Heat Evolution Curves in Dam Blocks (Curve Designations are Shown in Table 2.18).

TABLE 2.18. CHARACTERISTICS OF THE BLOCKS (ACCOMPANYING FIGURE 2.7)

No. of the curve on the figure	Height of the block, m	Initial temp. of the concrete mixture, °C	Cement	Cement consumption, kg/m <sup>3</sup>	Date of placement
1	6	7,2	Slag portland cement	240	29/XII
2	5,5	10	"	240	17/XI
3	3	14	"	240	22/XI
4	3	3	"	240	31/X
5	3	6	Portland cement	320	26/X

When concreting such massive blocks even in winter the concrete temperature exceeds the temperature of the concrete mixture when it is placed for a long period of time. Heated mold work is necessary primarily to premature cooling and freezing the external layers of the block concrete. Heated mold work promotes equalization of temperature fields within the concrete mass and reduction of temperature gradients between internal and external concrete layers.

The nature of exchange processes which occur between the concrete and surrounding medium depend largely on the thermal treatment conditions. Thermal and mass transfer phenomena in the material drying process were studied by A. V. Lykov. He suggested a system of differential equations to compute the processes taking place. Processes which are different than those which occur in drying of the materials take place in concrete due to heat liberation during hardening and binding of water during thermal treatment. The moisture content of the cement mixture is more than the hygroscopic, therefore the phase transformations which occur when drying the materials are absent within the part at a temperature below  $100^{\circ}\text{C}$ .

During thermal treatment a great deal of heat which must be considered in the energy balance of the heat consumed in heating the products is liberated from the concrete during the first few hours. Temperatures which considerably exceed the temperature of the medium and product surface develop within the concrete slab due to the exothermicity of the cement. Consequently, hardening conditions which differ from those calculated are produced and considerable temperature gradients arise which may cause the formation of cracks in the products.

In portland cement concrete the liberation of heat during heat-up may reach values which correspond to a  $70\text{--}80^{\circ}\text{C}$  concrete temperature rise due to exothermic heat. In doing this irregular temperature fields and a change in moisture conditions in the concrete are observed. Therefore the conditions and duration of thermal treatments should be fixed and controlled with consideration of self-heating of the concrete.

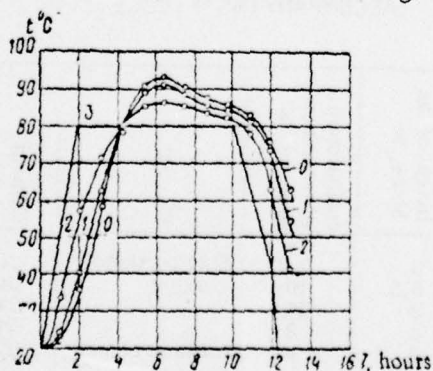


Figure 2.8. Time Change of the Temperature of Ordinary Portland Cement Concrete in Various Cross-Sections of a Reinforced Concrete Slab 24 cm Thick. 0, 1, 2, In the center, in one-fourth of the thickness and on the surface of the slab respectively; 3, Temperature of the medium in a chamber.



Figure 2.8 shows the change in concrete temperature in time in slabs 24 cm thick heated in a chamber at 80°C. As was shown in work [17], small-scale structures can heat up no more than 3-4 hours at 80°C. Further heating of slabs or similar members may occur without supplying heat or in heated piles by two-stage heating. The question of the concrete cooling rate and temperature gradient drop arises in heating massive parts.

The data obtained by L. Chumadova in studying six portland cements at the Leningrad Polytechnic Institute can be used to calculate heat liberation during thermal treatment of concrete and reinforced concrete members and structures. The results of her studies on determining the amount of isothermic specific heat liberation of cements in concretes are shown in Table 2.19. The concrete mixtures were prepared using 330 kg/m<sup>3</sup> cement, with a W/C = 0.45 and 2 cm slump. The heat liberation was determined at 20, 40, 70 and 80°C in hardening times beginning with 5-18 hours, ending with 36-168 hours.

TABLE 2.19. SPECIFIC EXOTHERMAL HEAT LIBERATION OF CEMENTS IN CONCRETES, kJ/kg

Hardening temp., °C	Hardening time, hours	Cements					
		Alekseyev	Belgorod	Lenin-grad	Volga	Sebrya-kov	Pikalev
20	18	69.9	121.8	86.7	71.2	66.9	70.3
	24	94.2	137.8	110.5	92.5	84.6	93.8
	48	141.1	185.1	148.6	135.7	128.1	164.5
	72	161.2	213.1	176.7	164.9	144	193.5
	96	173.4	233.6	198.9	183.8	190.1	212.7
	120	191.3	252.1	217.3	203.5	209.4	229
	144	198	267.5	225.3	—	—	244.5
	168	209.4	285.6	242.4	—	—	260
40	6	59.5	108	96.7	54.4	64.5	100.1
	18	140.7	197.6	200.9	141.5	142.4	184.6
	24	161.2	219.8	231.1	162.9	169.2	213.1
	48	210.2	272.2	293.9	218.1	220.7	270.5
	72	239.1	308.2	328.3	249.1	246.2	299.4
	96	263.4	329.5	355.1	274.7	262.9	321.6
	120	240.3	339.1	367.6	290.6	275.5	335.8
	144	297.3	348.8	380.6	304.4	285.9	349.2
70	5	89.6	151.9	114.3	73.7	88.8	—
	9	144	196.8	167.5	151.6	139.4	151.2
	18	195.9	253.7	215.6	211.9	178.8	215.6
	24	213.1	217.3	231.1	231.9	198	238.7
80	5	—	—	133.1	—	—	66.2
	9	—	—	195.5	—	—	160.8
	18	—	—	255.4	—	—	232.4
	24	—	—	276.8	—	—	257.5
	36	—	—	289.3	—	—	278.4

Commas indicate decimal points.

Concretes are used at low sub-zero and at high above-zero temperatures. Therefore it is necessary that the heat liberation of cement be considered with regard to some specific conditions. During freezing temperatures heat liberation proceeds slowly, and rapidly during electrical curing, steam curing, even more in electrical heating of the mixture. During winter concreting the use of cements with the property of rapid and high temperature liberation is desirable in order to provide favorable hygrothermal conditions for a concrete before it acquires the necessary strength by the instant it freezes.

Heat liberation must be controlled to prevent the appearance of cracks when concreting massive hydrotechnical structures, furnace, hot-blast stove, and stack foundations, and so forth. When manufacturing prefabricated concrete and reinforced concrete products and structures, heat liberation must be taken into consideration from the point of view of energy resources and the prevention of concrete drying when its temperature exceeds the temperature of the chamber or other thermal unit (especially at  $t = 100^{\circ}\text{C}$ ). Even under dry and hot climatic conditions it is necessary to consider the heat liberation of cement during placement and concrete curing in various structures and facilities. In some cases it may cause overheating, drying and crack formations in structures.

Automatic control of thermal processing conditions at prefabricated reinforced concrete factories is erratic. Usually the temperature in the steam curing chambers is controlled and during isothermic curing the temperature of the concrete in the products exceeds the temperature of the medium in the chamber by several degrees for 4-6 hours. During this time moisture begins to be lost. For heavy concrete these conditions are not optimum. Therefore the temperature of the chamber medium must be corrected in terms of concrete temperature. Heat liberation should be used by builders as an additional energy reserve.

#### Structure of Cement Stone.

During the initial hardening period a cement paste is regarded as a capillary porous body which consists of solid, liquid and gaseous (the presence of entrained air) phases. During this period it is plastic and therefore its strength is determined by various types of plastometries. The nature of the porous structure of the hardened cement stone determines the basic properties of the concrete -- strength, deformability, permeability, frost resistance. An enormous amount of research is devoted to questions of studying the micro- and macrostructure of cement stone and concrete. The microstructure is studied using electron microscopy; x-ray diffraction analysis is used to determine the composition of highly dispersed new crystal formations. The porosity of cement stone is determined using various methods, including nitrogen absorption and a mercury porosimeter which make it possible to examine the structure of the material on the molecular level.

The properties of concrete are largely determined by its macrostructure. Concrete macrostructure is defined as the totality of all its structural elements: coarse and fine aggregates, crystalline concretions

of new formations, the presence and dimensions of pores and capillaries in its structure. The quantitative ratios of individual elements and their interrelationship are determined by using various physical, physical-chemical and mechanical methods.

Thermal treatment and freezing at the early stage of hardening have a great effect on the formation of the structure of cement stone and concrete.

It has been established on the basis of studies conducted together with the physical-chemical laboratory of the Scientific Research Institute of Concrete and Reinforced Concrete that when concrete is frozen at an early age, defects are observed only in the macrostructure, i.e., in pores with a radius of more than 1  $\mu$ . When samples are frozen in a chamber at  $-20^{\circ}\text{C}$ , no disruptions in the gel structure are observed when the preparations are scanned under an electron microscope with magnification 10,000X. Similar results have been obtained in determining the porosity of cement stone and concretes using water absorption and ordinary microscopy methods. The mineralogical content of the cements affects the formation of the structure and the kinetics of strengthening of cement stone and concrete to a large degree.

Alite cement concretes with an increased content of  $\text{C}_3\text{A}$  (a type of Nevyansk cement) are characterized by more rapid hardening in the initial periods. Acceleration of cement hydration processes is associated with the development of heat liberation and the creation of favorable conditions for the formation of a dense and stable structure which imparts to the concrete the ability to resist the damaging effect of sub-zero temperatures. At optimum temperatures the hydration processes of high alite cements with a large content of  $\text{C}_3\text{A}$  proceed more smoothly and the rapid agglomeration of gels is accompanied by the occurrence of contraction pores ( $r < 0.1 \mu$ ) in which water freezes below  $-40^{\circ}\text{C}$ .

Professor T. Powers of the Portland Cement Association of the U.S.A. has devoted a great deal of attention to studying the microstructure of new cement formations. He presented a simplified model which depicts the structure of a cement gel (hardened paste) at the First International Symposium on Winter Concreting in 1956 in Copenhagen.

Figure 2.9 shows gel particles in the form of spherulites with air and larger pores formed as the result of the contraction of the hardening cement gel [83].

Ideas about the forming structure of a cement gel have changed somewhat as the result of the physical-chemical studies conducted by T. Powers. At a symposium on the structure of cement stone and concrete held in Washington in 1965, T. Powers reported that the most modern research methods have led to a change in conceptions of the structure of cement stone and the products of new formations. Not spherulite-like particles, but foliated, felt-like and reticulate crystals are the basic



structures of the elements [84]. This new model of the structure of a hardened cement paste is shown in Figure 2.10.

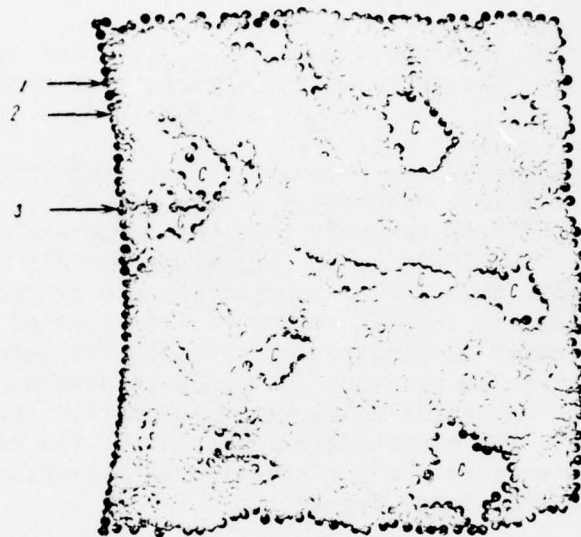


Figure 2.9. Simplified Model of the Structure of Cement Paste Suggested by T. Powers. 1, Gel particles; 2, Gel pore; 3, Particle boundary of an air pore; C, Contraction pores.

Similar ideas about the structure of cement stone have been stated by other researchers. It may be considered generally accepted that hydrate compounds with a crystalline structure are formed from cement-water suspensions. A stony structure is created with the passage of time from the hydrate compounds formed at the beginning of hardening. The formation of a dense cement stone structure depends on the W/C, i.e., on the thickness of the cement paste, the fineness of the grinding and mineralogy of the cement, favorable hygrothermal conditions for hardening, the introduction of mineral and chemical additives. The greater the water-cement ratio, the greater the total and capillary porosity and accordingly the shrinkage as well as the destructive processes in heating and freezing cement stone and concrete.

Since we cannot discuss the presentation of experimental data on cement stone structure in detail, we shall give only a short description of the processes which occur and the classification of concrete porosity accepted by us.

When cement is mixed with water, its hydration and the formation of the initial coagulation structure which acquires plastic properties begin. These properties are customarily characterized as plastic strength. The determination of setting times is the universally accepted standard test of the mechanical properties of a cement paste of normal thickness. The plasticity of cement paste corresponds to the beginning and period of its

setting. The crystallization structure has already been formed by the time setting is completed. The forming cement stone rapidly begins to acquire strength which is measured not in grams, but in kilograms per square centimeter. The crystals of the new formations coalesce and the initial skeleton is overgrown with very fine particles of calcium hydrosilicate. The crystal lattice of the calcium hydrosilicates consists of layers formed by silicate tetrahedrons of  $\text{SiO}_4$ . They are joined by a common oxygen ion along the length of the crystal, thus forming networks. Each two layers of  $\text{SiO}_4$  tetrahedrons joined by calcium ions form a layer of hydrosilicate. Several layers comprise laminae of calcium hydrosilicate. Losses or water saturation is accompanied by a change in the distance between layers of the hydrosilicate crystal lattice. Shrinkage and swelling of the gel when the temperature and humidity of the ambient medium changes are associated with this. A model of a structure comprised of calcium hydrosilicate is shown in Figure 2.11 [37, 84].

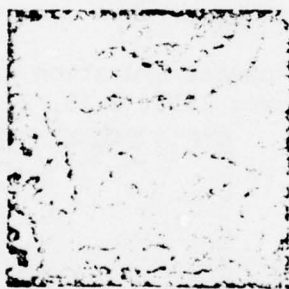


Figure 2.10. Cement Gel Model  
Proposed by T. Powers. K, Contraction  
pores.

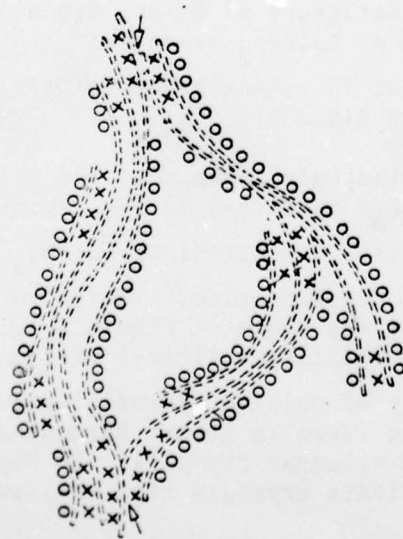


Figure 2.11. Model of the Structure of Calcium Hydrosilicate  
Proposed by R. F. Feldman and P. G. Sereda. ==, Hydrosilicate  
layers; X, interlayer of water; O, Adsorbed water.

As the results of x-ray diffraction analysis show, it is very difficult to distinguish CSH (I) from CSH (II). In contrast to x-ray diffraction patterns of natural crystalline hydrosilicate, tobermorite [sic], they have only few images. CSH (I) has a greater capacity for shrinking and swelling than CSH (II).

Z. M. Larionova of the Scientific Research Institute of Concrete and Reinforced Concrete is studying the hydration processes of the minerals of portland cement clinker and cement using a complex of modern methods. These studies are interesting in that they are being conducted in conjunction with technological studies of cement and concrete hardening at above-zero and sub-zero temperatures; this will make it possible to scientifically substantiate the results obtained and establish a relationship between the mineralogical content of the cements used and the kinetics of concrete strengthening under various hardening temperature conditions. Physical-chemical studies being conducted along with technological studies are becoming more objective, since they aid technologists in understanding the mechanism of those processes which occur when concretes harden.

Microphotographs of portland cement hydration products taken by Z. M. Larionova are shown in Figures 2.12, 2.13, 2.14.



Figure 2.12. Structure of Cement Stone.  
a, Aggregation of  $\text{Ca(OH)}_2$  crystals;  
b, Hydrated mass in cement stone (platinic-carbon replicas  $\times 10,000$ ).

These studies have convincingly shown that the calcium hydroxide formed during hydration of  $\text{C}_3\text{S}$  is formed in the cement stone in the form of comparatively large crystals. Crystals of  $\text{Ca(OH)}_2$  are shaped like hexagonal plates in lateral cross-section. They form agglomerations by piling on top of one another (as shown in Figure 2.12, a, longitudinal cross-section). A gel-like (microcrystalline) mass between the  $\text{Ca(OH)}_2$  crystals is comprised mainly of calcium hydrosilicate. In low-density sections of the cement stone (even in normal hardening samples) the calcium hydrosilicates form columnar crystals. In Figure 2.12, b, it is clear that calcium hydrosilicate crystals fill the cement stone pores.





Figure 2.13.  $C_3A$  Hydration Products. a, Under normal conditions; b, With thermal treatment (platinic-carbon replicas X10,000).



Figure 2.14. Calcium Hydrosulfoaluminate Crystals (Ettringite). a, In a pore; b, In the cement stone mass (platinic-carbon replicas X10,000).

When  $C_3A$  is hydrated, a number of calcium hydroaluminates is formed, the composition of which depends on technological factors. This mineral is hydrated without liberating free  $Ca(OH)_2$ , and the hydrates which emerge form fine crystals.

For portland cement stone (in which the liquid phase is supersaturated by calcium ions)  $C_4AH_{13}$  is the typical calcium hydroaluminate (Figure 2.13, a). When cement stone is thermally treated hexagonal  $C_4AH_{13}$  becomes cubic  $C_3AH_6$  (Figure 2.13, b). In doing this octahedral grains crystallize instead of fine hexagonal plates.

In the presence of gypsum which is a necessary component of factory cement, calcium hydrosulfoaluminate in the trisulfate form  $3CaO \cdot Al_2O_3 \cdot 3CaSiO_3 \cdot 31H_2O$  occurs. The sulfoaluminate forms fine needle-like crystals in low-density sections of the cement stone (Figure 2.14, a).

In contrast to  $C_3A$ , tetracalcium aluminoferrite  $C_4AF$  hydrates with the liberation of free  $Ca(OH)_2$ , and a certain amount of  $Fe_2O_3$  is included in the hydrates. Upon thermal processing a hexagonal hydrate becomes cubic (the same with the inclusion of  $Fe_2O_3$ ). The hydrate may decompose with the liberation of free  $Ca(OH)_2$  and  $Fe_2O_3$  when treated for a prolonged period of time in an autoclave.

Figure 2.14, b, shows an electron microphotograph (X10,000) of cement stone in which the hydrosilicate mass, needle-like crystals of calcium sulfoaluminate and coarse folia of calcium oxide hydrate (left) are clearly visible.

During the hardening of cement stone important structural changes occur spontaneously as well as under the influence of various physical-chemical and technological factors. Knowledge of the special features of the formation of a cement stone structure make it possible to explain many phenomena which occur when the concrete structure is formed.

In conjunction with this the phenomenon of contraction of cement stone which largely determines the contraction of concrete and unavoidable structural changes in it is of interest. Our studies of the changes which occur in the structure at the early stage of hardening using various methods of hygrothermal treatment have drawn attention to the importance of plastic contraction.

As a rule, researchers study concrete contraction in accordance with the standard method by passing the initial stage of its passage, i.e., plastic contraction. It must be noted that both here in the Soviet Union as well as abroad various authors define and explain contraction in various ways. Some scientists regard concrete as a homogenous isotropic



body. In actuality, concrete contains a heterogenous structure and its texture is diverse. With regard to microstructure, the contraction of cement stone must be regarded in connection with volumetric changes in the cement gel. Gel contraction (interlayer) is measured in several angstroms (less than 50 Å). Capillary contraction is determined at 35% relative air humidity for 7 days or in terms of moisture loss at a temperature of 105°C. This contraction is measured by values such as 50-1000 Å. Moisture contraction is defined as the expulsion of free water from the pores.

Interlayer contraction of the gel may be graphically explained by the model of a calcium hydrosilicate cell proposed by R. F. Sereda and P. G. Feldman shown in Figure 2.11. The density and structure of the pores depend largely on technological factors.

We accept the following classification of pores in cement stone and concrete:

- ultramicropores (gel pores) with a radius of up to 0.01  $\mu$ ;

- micropores (contraction and microcapillary pores) with a radius of from 0.01 to 0.1  $\mu$ ;

- macropores (transition and larger capillaries) with a radius of from 0.1 to 1  $\mu$ ;

- large pores with a radius of more than 1  $\mu$  (more than 10,000 Å);

- large pores and cavities which form in the concrete under grains of coarse aggregate of a sedimentation nature due to air entrainment and to the varied degree of consolidation of the concrete during placement.

Large pores in concrete may be measured also in millimeters. According to the data of A. Ye. Sheykin, capillaries with a radius of up to 0.1  $\mu$  eventually lead to extensive contraction in cement stone and concrete. The moisture in them is retained by capillary forces. During plastic contraction the free water is expelled when capillary forces do not yet appear in the concrete.

This contraction is characteristic for placing concrete or mortar in a dry medium at high temperatures. Questions of structural changes, including contraction and temperature deformations, are examined in Chapters 4-6 in conjunction with temperature and moisture conditions for concrete hardening.

## Effect of an Electromagnetic Field on Processes of Hydration and Structural Formation of Cement Stone.

Searches for new means of using electrical energy have led to the development of the induction method of electrical heating or external heating (radiated and convection transmission of heat). In conjunction with this there has arisen the necessity of studying the action of an electric current and an electromagnetic field on the processes of hydration and structural formation of cement stone and concrete regardless of the thermal factor.

In the early stages of hardening a cement paste or concrete mixture may be regarded as a colloid system with a dispersed solid and liquid phase in the form of an aqueous solution saturated with regard to the initial cement. By analogy with any colloid, in a cement paste or concrete mixture there is a dipole electrical layer which charges the particles on the boundary of the two phases (solid and liquid).

The nature of the action of the variable electromagnetic field is basically resonant. This means that charged particles will move in an oscillatory manner in aqueous suspensions of clinker minerals or in cement paste. The rate of oscillatory motion depends primarily on the intensity of the electromagnetic field, the current frequency and dimensions of the charged particles. In addition, coulomb forces of the attraction of opposite charges are at work in the solution; this reduces the active force of the electromagnetic field.

In some studies carried out here and abroad it is pointed out that in aqueous colloid systems oscillation of solid phase particles and their orientation with regard to the lines of magnetic force are observed by the action of a variable electrical current.

Studies were conducted at the Scientific Research Institute of Concrete and Reinforced Concrete on the effect of the transient action of a variable electromagnetic field on the composition and nature of crystallization of new formations in hydration of gypsum, individual clinker minerals and cements from the beginning of mixing to setting. Hemi-hydrous gypsum, alite, alumoferrite, high aluminate clinker and portland cement from the Voskresenskiy Factory were used as the starting materials. Special units which created a magnetic field in a space where a microscope and objective were positioned were built to conduct the experiments. These units were developed and constructed at the Department of Electrical Engineering and Electrical Equipment of the All Union Correspondence Construction Engineering Institute with the participation of A. A. Altukhov. A study using petrographic and x-ray diffraction analyses and electron microscopy were carried out in the physics-chemistry laboratory.

Four coils superimposed on one another and connected in parallel comprised the first unit designed to create an electromagnetic field. The coils were connected to a power alternating current through a voltage regulator. At first the tests were conducted with a low strength

electromagnetic field (approximately 20 oersteds). The strength of the field was constant during the experiment; it was determined using a measuring coil and voltmeter.

Polarization microscope MIN-4 and a photoadapter were positioned in the space enclosed within the coils. A second identical microscope was located outside the field at the same location. Specially prepared slides were used for microscopic examination. To do this a drop of the cement-water suspension was placed on the objective glass, spread in a thin layer, covered with glass and sealed with cement. It was necessary to seal the slide in order to avoid water evaporation and carbonization of the cement hydration products. The slides were photographed at 5, 10, 15, 20, 30, 60 and 120 minutes during the experiment.

During the experiments it was necessary to ascertain the differences in the rate of occurrence, the dimensions, the quantity and orientation of the crystals of the new formations during mineral and cement hydration under normal conditions and in an electromagnetic field. Slides of a suspension of hemi-hydrous gypsum with a 1:10 gypsum-water mass ratio were most suitable for these purposes. Hemi-hydrous gypsum  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  is characterized by ready and rapid solubility in water. When supersaturation was achieved, oblong prismatic crystals of dihydrous gypsum began to crystallize out of the solution.

Tests conducted with the first unit showed no differences in the nature of hydration of hemi-hydrous gypsum, therefore it became necessary to increase the strength of the magnetic field. To do this a new unit was designed which differed from the first in that the numbers of turns was increased in its coils and the strength of the magnetic field reached  $75 \cdot 10^3$  A/m. But, considering the dispersion of the magnetic field and the possibility of overheating the system, the strength of the magnetic field actually used was no more than  $62.5 \cdot 10^3$  A/m.

A suspension of hemi-hydrous gypsum was also used as the principal subject in working with this unit. The effect of the action of the field could not be shown from analysis of tests repeated several times.

Since we did not obtain a clearly pronounced effect of the electromagnetic field using the first two units, we increased the strength of the electromagnetic field considerably and concentrated it on the subject. To do this a unit different from the first two was designed which comprised a transformer with an air gap in the core (Figure 2.15). Two transformer windings were interconnected in parallel and switched into an A.C. network. By regulating the voltage in the air gap of the coil it was possible to produce a variable magnetic field with a strength of approximately  $160 \cdot 10^3$  A/m. By reducing the area of the ends of the coil the strength of the electromagnetic field was increased to  $1000 \cdot 10^3$  A/m. During the test the slide was inserted into the coil gap and then it was studied and photographed with a microscope. The other slide, the control sample, was held outside the effective area of the field.



Besides the suspension of hemi-hydrous gypsum, aqueous suspensions of aluminoferrite, alite, high aluminate clinker and portland cement from the Voskresenskiy Factory were used when conducting tests with the third unit.

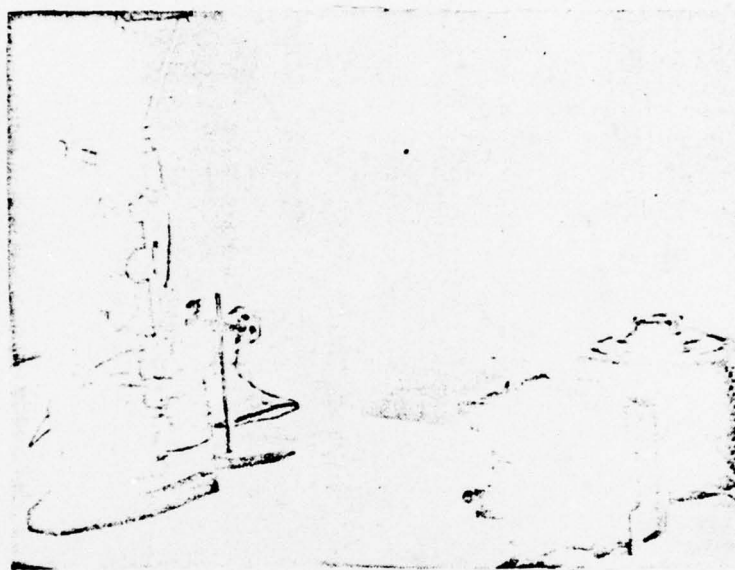


Figure 2.15. General View of the Electromagnetic Unit.

Just as in working with the first two devices, cylindrical crystals of bi-hydrous gypsum are formed in the suspension with hemi-hydrous gypsum which was subject to the action of the electromagnetic field and in the suspension outside it. No changes in the rate of crystal formation, direction, their quantity and dimensions were observed (Figure 2.16). The effect of the action of the electromagnetic field is even less probable in thick pastes.

The effect of the action of the electromagnetic field could have been expected when using the iron containing mineral aluminoferrite. But when comparing slides under normal conditions and those subject to the action of the electromagnetic field, the formation of needle-like crystals of calcium hydroaluminate confined to the unhydrated grains of  $C_4AF$  was observed in the form of indistinctly pronounced spherulites. No directivity in the distribution of the iron containing component of the aluminoferrite is observed during the action of the electromagnetic field.

In the same aqueous suspensions with alite (1:20 by mass) crystal growth proceeds more slowly. In the  $C_3S$  hydration process, shells of gel-like calcium hydrosilicate and hexagonal crystals of  $Ca(OH)_2$  are formed around the unhydrated grains. The formation of  $Ca(OH)_2$  crystals begins 5-6 hours after mixing, and therefore two test series were

Some slides were subjected to the action of the electromagnetic field immediately after mixing, other six hours later. When comparing them with slides outside the magnetic field, no differences were observed. In both slides the presence of large hexagonal folia of calcium oxide hydrate is noted among the hydration products after one hour.

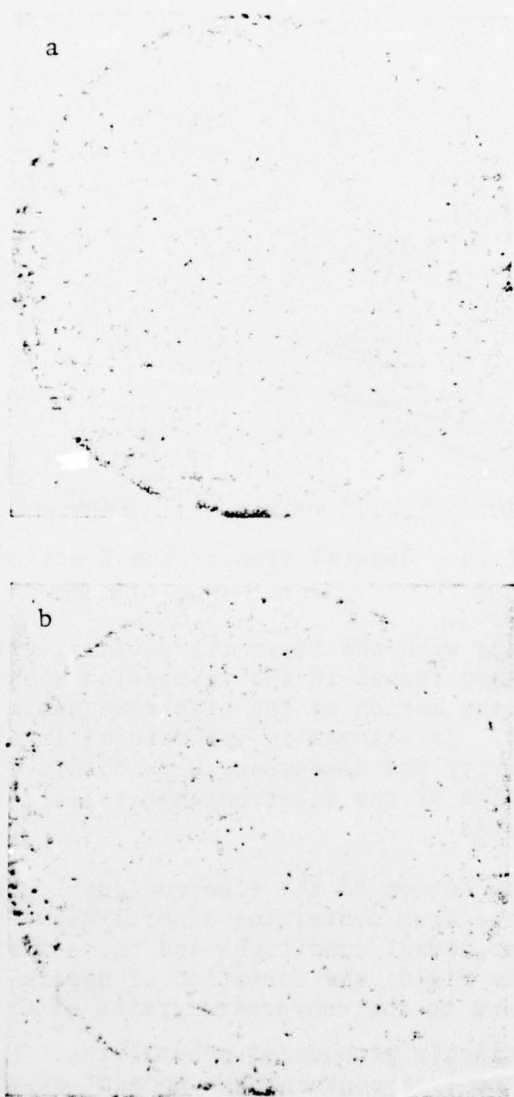


Figure 2.16. Gypsum Hydration Products During 30 Minutes.  
a, In an electromagnetic field of strength  $50 \cdot 10^3$  A/m;  
b, Without the field (slides magnified X300).

A study of the effect of an electromagnetic field on the hydration process of clinker and factory cements was the next stage in the research. High aluminate clinker ( $C_3S = 63.65\%$ ;  $\beta-C_2S = 15.85\%$ ;  $C_3A = 14.44\%$ ;  $C_4AF = 4.83\%$ ) and factory portland cement ( $C_3S = 56.82\%$ ;  $\beta-C_2S = 18.02\%$ ;  $C_3A = 8.71\%$ ;  $C_4AF = 14.82\%$ ) were used. When using high aluminate clinker 10% building gypsum was added. Cement-water suspensions and slides were prepared from this mixture. A large number of tests were carried out to choose the optimum concentrations of the suspensions and the time of electromagnetic field action.

It was ascertained that a suspension with a cement:water ratio of 1:20 (by mass) was most suitable in this work. In more concentrated suspensions crystals of new formations are too small. In more dilute suspensions the number of crystals of new formations is small and they appear considerably later.

Spherulite formations of calcium hydrosulfoaluminate  $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$  appear in 5-8 minutes when a mixture of high aluminate clinker is mixed with 10% gypsum in water. The action of the field began 5 minutes after mixing and continued for 3 hours. If we compare the suspensions of high aluminate clinker with 10% gypsum added subject and not subject to the action of the electromagnetic field, in both cases clearly pronounced spherulites of needle-like crystals of calcium hydrosulfoaluminate are formed around the grains (Figure 2.17). The apparent difference in the amount of ettringite is associated with gypsum grain size and suspension concentration.

No differences in the hydration process in the creation of crystals of new formations compared to a normal hardening preparation were observed when a suspension of portland cement from the Voskresenskiy Factory was exposed to the action of an electromagnetic field.

Electron microscopy and x-ray diffraction analysis were used for more detailed study of the effect of an electromagnetic field on the composition and structure of highly dispersed new formations.

The structure of a chip from hydrated samples of  $C_3S$  and  $C_4AF$  and Voskresenskiy cement ( $W/C = 0.5$ ) at age one day was studied under an electron microscope using the single-stage platonic-carbon replica method. Normal hardening samples were compared to samples exposed to the action of a variable electromagnetic field of frequency 50 Hz, and strength  $750 \cdot 10^3$  A/m for four hours, beginning at the instant of mixing.

In both cases the hydration products and the sample structure were identical. Sections of grains of  $C_3S$  covered with fine needle-like crystals of calcium hydrosilicate  $C_2SH_2$  are visible on the chipped surface in hydrated samples of  $C_3S$ . Hexagonal crystals of calcium hydroaluminate are



observed in hydrated samples of  $C_4AF$ . In samples of Voskresenskiy portland cement the surface of the chip is represented by fine needle-like crystals of calcium hydrosilicate  $C_2SH_2$  with zones having an amorphous structure which are similar in shape to the products of hydration of  $C_3S$ .

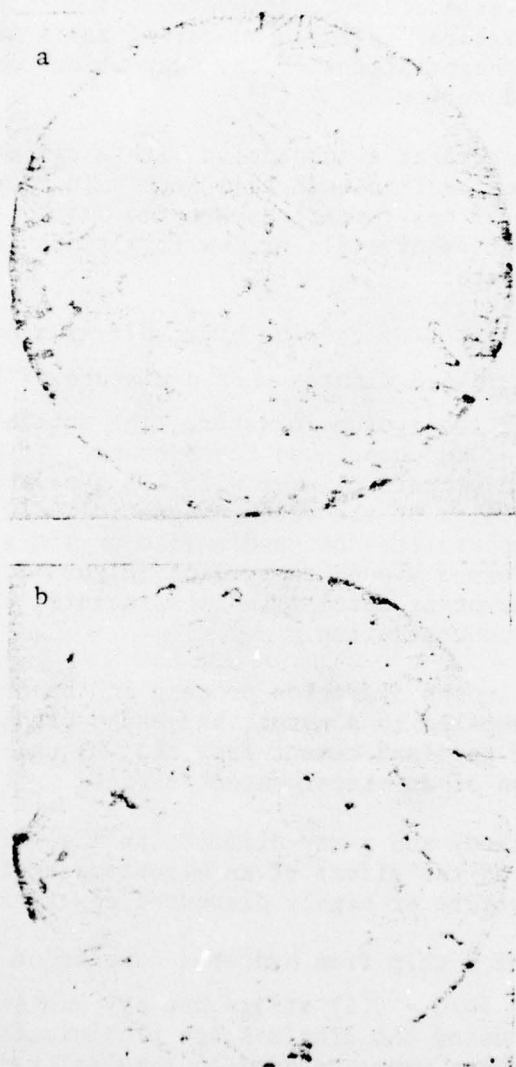


Figure 2.17. Products of Hydration of High Aluminate Clinker With 10% Gypsum 3 Hours After Mixing. a, Exposed to the action of an electromagnetic field with strength  $100 \cdot 10^3$  A/m; b, Without the field (slides X300).

In addition to electron microscopy, x-ray diffraction analysis was used to determine the composition of the highly dispersed crystal new formations. Powdered samples of hydrated clinker minerals and Voskresenskiy cement with a W/C = 0.5 at age one day were studied for this purpose. Some of these samples hardened under normal conditions, and others were exposed to the action of a variable electromagnetic field of strength  $750 \cdot 10^3$  A/m for four hours, beginning at the instant of mixing.

The use of such precise methods as electron microscopy and x-ray diffraction analysis has shown that no changes are observed in the composition of highly dispersed new formations. If the resonance nature of the variable electromagnetic field affected the rate of dissolution of the clinker minerals by the oscillatory movements of charged particles, differences in the ratios of  $\text{CaO}:\text{SiO}_2$ ,  $\text{CaO}:\text{Al}_2\text{O}_3$  and in the degree of supersaturation in mortars under normal conditions and those subject to the action of an electromagnetic field could have been expected. This in turn would lead to the formation of calcium hydrosilicates and hydro-aluminates of varying alkalinity, but such differences are not observed according to the data of electron microscopy and x-ray diffraction analysis.

Thus, the work conducted has demonstrated that although a theoretically variable electromagnetic field may lead to oscillatory movements of charged particles in cement paste and a concrete mixture, in actuality no changes in the phase composition, rate of growth of new formation crystals, their dimensions, shape and orientation were observed under the action of an electromagnetic field of strength from 20 to 4000 oersteds during hydration of clinker minerals and cement. The unevenness in distribution of clinker minerals in the cement paste and suspension and the temperature gradients during electric thermal treatment exert a considerably greater effect on the change in the formation of the crystalline structure of the cement stone.

Consequently, as noted previously with regard to the electrode method of heating, in this case the cement is warmed up by heat, and the action of an electromagnetic field has no effect within the parameters used. Let us note that, on the basis of repeated studies of the physical-mechanical properties of concretes having undergone various methods of thermal treatment, the modulus of elasticity usually drops 15% after electric heating in construction standards. This is caused by the unevenness of the distribution of electrical, thermal and moisture fields in the structures.

In many cases by age 28 days the strength indices of concrete heated by an electric current do not reach full value compared to concrete hardened under normal conditions. Therefore the creation of favorable equal hygrothermal conditions is necessary in all methods of electric thermal treatment, including that in an electromagnetic field. This is confirmed by observations of the condition of flat reinforced concrete slabs having undergone thermal treatment in an electromagnetic chamber at a house construction combine in Minsk. Slabs above and below the

block differed from those in the middle after passing through the treatment cycle with regard to color and moisture. This is explained by the shielding of the current when heating the slabs within the block.



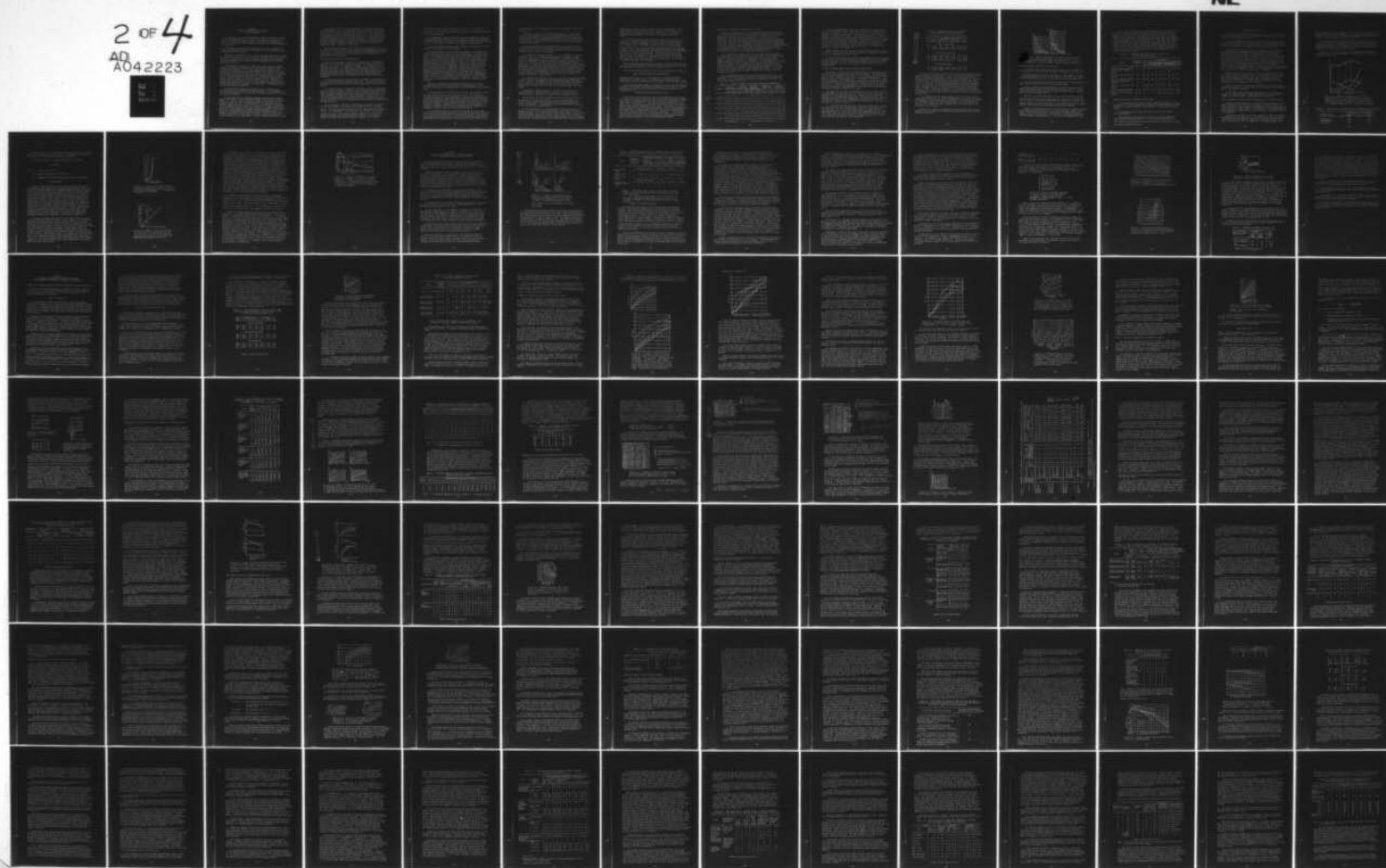
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### CHAPTER 3 SETTING TIMES AND PLASTIC STRENGTH OF A CEMENT PASTE

In the capacity of a building material, cement is ordinarily used as the most important component of concretes and mortars of various types as well as of asbestos cement articles. Cementing, the plugging of wells and certain other special operations in which it is used independently are an exception.

In addition to strength and other characteristics, requirements for cement in international standards with regard to setting times of cement paste must also be set forth.

Builders are interested not only in the strength properties of cement, but also in such characteristics as standard consistency and setting times, the plastic properties of a paste and plastic strength, heat liberation, electrical conductivity and certain others associated with the manifold conditions of its use.

The rheological properties of mortar and concrete mixtures depend largely on the plastic properties of the cement paste and the kinetics of the structural formation of the cement stone during hardening. The application of mechanical forces when manufacturing elements and building facilities as well as thermal action on cement to accelerate its hardening are directly associated with the structure forming properties of cement paste. Therefore mechanical and heat action during the formation of a strong structure leads to irreversible changes; this is reflected in the physical mechanical properties of the cement (concrete). Freezing of a cement paste (concrete) at an early age also causes irreversible processes in the formation of the structure, and consequently in the formation of construction-technical properties.

According to the requirements of GOST 310-60 for cements, when testing the latter in a paste of standard thickness, at a temperature of 20°C setting should begin no earlier than 45 minutes, and end no later than 12 hours after pouring.

The requirements of the standard regarding setting times of cement imply, as it were, a certain rejection minimum of the quality of factory production. However, these requirements cannot be approached from the mechanical aspect nor can the setting times of concretes and mortars be directly judged from them. Setting times may vary considerably depending on the temperature, water-cement ratio, workability of the mixture, and additives. The diverse ways of using concretes and mortars in construction levy various requirements for cement setting and hardening times. For example, in factories which make prefabricated reinforced concrete parts, the most rapid removal of the forms is ensured either by using stiff concrete mixtures or by accelerating the cement hardening and setting times.

During winter and fall-spring operations a temperature drop results in the retardation of setting time; this affects especially mixed cements. Therefore in these cases it is necessary to resort to various methods of accelerating the cement hardening and setting times. On the other hand, during operations under high temperature conditions and when transporting a concrete and mortar mixture over great distances, the problem of taking measures to retard cement setting times often arises. The rapidity of setting of portland cements is associated primarily with the tricalcium aluminate content. To prevent setting from ending 5-10 minutes after making the cements, gypsum is added to them.

When using factory cements of various types in construction, it is necessary to be able to control their setting and hardening times as needed. To do this it is necessary to know the nature of the phenomena which cause cement setting and expose the factors which lead to acceleration or retardation of setting times.

#### Physical-Chemical Nature of Cement Setting.

Setting and hardening of cement are complex physical and chemical processes. During setting a cement paste gradually loses plasticity and thickens, thus acquiring a negligible strength. The hardening process which then develops, i.e., conversion of cement paste into cement stone, continues for several years under favorable hygrothermal conditions. The structure and strength which form in doing this by the cohesion between individual particles of new formations as well as between these new formations and the surfaces of the aggregate grains, form a monolithic solid body.

A reaction between the clinker minerals and water on the particle surface occurs first when the cement and water join. The process of water's interaction with the clinker minerals may be represented in the following manner.

All clinker minerals, no matter how low their solubility, immediately begin to dissolve in water. Hydrolysis (dissociation) of the minerals and their hydration (joining with water) occurs in an aqueous solution. The hydrate compounds being formed create supersaturated solutions from which these compounds precipitate in a finely dispersed, colloidal state. It is this circumstance which explains the plasticity of cement paste which has an alkaline reaction as a consequence of the appearance of hydrolytically forming free lime.

The occurrence of free lime in cement paste is caused by hydrolysis of the basic compound -  $C_3S$  which is an unstable system in an aqueous medium. Colloidal bicalcium hydrosilicate also forms during the hydrolysis of  $C_3S$ . As a consequence of its extremely low solubility in water and increased stability this compound undergoes hydrolysis to a very small degree, and almost free calcium hydroxide is formed. In an aqueous solution  $C_3A$  hydrolyzes with the opposite compound of the initially



precipitated  $\text{Ca(OH)}_2$  and the subsequent hydration. As a result of dissolving, hydrolyzing and hydrating  $\text{C}_4\text{AF}$  yields tricalcium hydroaluminate and calcium hydroferrite.

The interaction of cement components with water begins from the grain surface and proceeds rather slowly. The products of hydrolysis and hydration which first occur in colloidal form create a plastic layer of gel which requires a large amount of water to form around the cement grains.

At first the cement paste is highly workable after mixing due to the presence of a large amount of free water.

The colloidization process of cement components is accompanied by a gradual increase in the viscosity of the cement paste. The swollen shells of the cement grains let water pass slowly, and therefore access of the latter to the deeper internal layers of the particles is hindered. When the gel absorbs a significant amount of water, the colloidal shell may separate from the main body of cement grains, as the result of which the water gains access to the non-hydrated layers of the clinker minerals, and the hydration process intensifies. In addition, water is drawn out of the gel shell within the cement grains continually, although slowly. All these processes cause a permanently continuing reduction in the amount of free water; this promotes an increase in the viscosity of the cement paste and leads to setting which is characterized outwardly by gradually increasing thickening of the cement paste and a deterioration in its pourability. The gradually increasing viscosity of the cement paste is conditionally characterized by the beginning and end of setting as well as by the increase in temperature, electrical conductivity and so forth.

Some of the products of hydrolysis and hydration of the clinker minerals remain in a colloidal state for a prolonged period of time. Calcium hydrosilicate is included among these new formations in the cement paste.

Such new formations as  $\text{Ca(OH)}_2$  and  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}$  gradually change from the colloidal state into a crystalline state. The crystalline compounds which occur in the cement paste in the form of sub-microscopic crystalline formations coalesce and yield a strongly developed network of crystalline concretions which cause the hardening cement stone to acquire mechanical strength. Thus we may consider that the primary cause of the increase in strength in cement mixed with water is the conversion of coagulation compounds into crystalline compounds and the formation of a mechanically strong skeleton of crystalline concretions.

The second most important reason for the hardening of the cement paste is the consolidation process of the hydrate new formations remaining in a colloid state (mainly gels of calcium hydrosilicate). This consolidation process of the colloid gel occurs due to water being drawn off by the internal non-hydrated layers of the particles and as a result of the

unavoidable process of aggregations of colloids which tend towards self-consolidation.

Thickening colloid gells which are permeated in all directions by the crystalline concretions are more strongly attached to the crystal surface and consequently also promote strengthening of the cement stone. This shrinkage of the crystalline concretions by the self-consolidating colloid gel may be regarded as the third cause of the strengthening of a hardening cement stone.

Surface carbonization which proceeds due to the carbon dioxide in the air and which leads to the formation of a more dense layer of calcium carbonate which prevents new penetration of gases and liquids into the cement stone is of accessory importance.

The setting and hardening process, i.e., the increase in strength of the cement stone, is a complex phenomenon which is dependent on many causes and circumstances. The following affect the cement hardening process: mineralogical content of the binder, degree of dispersion of its particles, admixtures of certain substances, temperature and moisture conditions. All these factors should always be considered during winter concreting for which those optimum conditions should be selected each time which would create the most favorable situation for the strengthening of the cement stone and if possible in the shortest time interval. In doing this the effect of the temperature factor on the rate of the processes which are occurring in the hardening cement stone, and consequently in concrete, must always be kept in mind.

The nature of the processes which occur during the setting of portland cement is revealed by determining the setting times of the individual clinker minerals. The ground tri- and bicalcium silicates, and sometimes even the tetracalcium aluminoferrite which are mixed with water set in approximately the same time as is observed in ordinary factory portland cements.

A completely different picture is observed in the setting of tricalcium aluminate. The setting of the latter in a paste of plastic consistency ends no more than 10 minutes from the instant of mixing.

In some cases tetracalcium aluminoferrite ( $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Se}_2\text{O}_3$ ) sets at the same rate as tricalcium aluminate. This may be explained by its rather intense hydration and the separation of tricalcium aluminate hydrate in doing this. Consequently, calcium aluminates play a decisive role in the setting of portland cement.

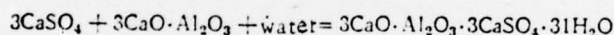
As is known from tests of portland cement without the addition of gypsum, its setting times begin approximately at the same rate as tricalcium aluminate, i.e., 3 hours and 5 minutes after mixing. The dilution of portland cement clinker with furnace slag, tripoli earth and other additives does not significantly affect cement setting. Thus, for example, when grinding slag portland cement and pozzuolanic portland cement without

added gypsum, they set just as rapidly as pure portland cement. When cement without added gypsum was being produced in the Urals during the years of the Great Patriotic War, it was necessary for the author to study developing measures for retarding the setting times of such cements.

To retard the setting times of portland cement (and its derivative cements), 3-5% gypsum is added to it at the factories during grinding. In this case a larger percentage of gypsum is added to cements with a high content of  $C_3A$ . The gypsum, which dissolves in water in amounts of approximately 0.2%, forms a compound with the precipitating tricalcium aluminate. As the cement hydrates, the calcium aluminate, which combines with the gypsum, precipitates from the solution in the form of an insoluble double salt -- calcium sulfoaluminate. This occurs until the gypsum reserve is able to compensate for the gypsum removed from the solution rapidly enough. The addition of gypsum must be regarded not only from the point of view of controlling the setting times of cement, but also as an inherent component of the hardening.

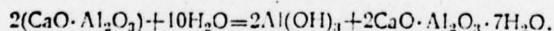
The increased grinding fineness and activity of modern cements as well as the use of steam curing of structures engender the necessity of increasing the amount of gypsum added at the factory (up to 5-8%).

The calcium hydrosulfoaluminate which forms according to the reaction



during the first hours, i.e., at the instant of structural formation, consolidates the cement stone by accelerating the hardening process. For this reason hardening accelerates and the strength of the concrete increases.

The setting of bauxite cement is caused by the fact that free aluminum hydroxide is liberated as the result of hydrolysis when bicalcium aluminate interacts with water and the hydroaluminate is formed according to the following reaction:



The aluminum oxide hydrate and bicalcium hydroaluminate being formed occur first in colloidal form in the form of a gel which gradually increases its viscosity by absorbing more and more of the water introduced into the cement mixture when making it. The bicalcium hydroaluminate which then passes into a crystalline state and forms crystalline concretions promotes rapid strengthening of hardening bauxite cement. Consequently, in bauxite cement setting is associated with the formation of a gel, and hardening with the appearance of a large number of crystals of bicalcium hydroaluminate which form a strong skeleton of crystalline concretions. No crystals of calcium hydroxide are observed in setting bauxite cement. Bauxite cement thus hardens as the result of the contraction of the aluminum oxide gels and the intense formation of calcium hydroaluminate crystals.



### The Effect of Temperature on Cement Setting Times.

Cements most characteristic of construction were taken for the tests. The tests were conducted with a paste of normal thickness, but at different temperatures which are of practical interest. The temperature of the cement paste reached the set air temperature, except for the cases at 50 and 70°C, when they were somewhat lower than the established experimental conditions. The established cement setting times at different temperatures are cited in Table 3.1. As is apparent from this table, as the temperature of the air (and cement paste) drops, the periods of the beginning and ending of setting diverged, and the entire cement setting period grows longer. At a temperature near 0°C, the beginning of cement setting is 2-4 times slower, and more, vis-a-vis the beginning of setting at 15°C.

As the temperature increases to 70°C the cement setting times are 3-6 times faster vis-a-vis the setting times at 15°C. At high temperatures the period from the beginning to the ending of setting drops sharply. The change in temperature involves an acceleration or retardation of the chemical reaction of cement-water interaction. As the temperature increases, hydrolysis (decomposition) of the principal minerals of cement clinker occurs more rapidly. The formation of the calcium hydrosilicate gel and the precipitation of the calcium hydroaluminate and calcium oxide hydrate crystals proceed more intensely as the temperature increases. The result of this is the acceleration of cement setting times and the increase in the paste viscosity.

As the temperature drops all these processes occur more slowly. The solubility of the calcium oxide, conversely, increases as the temperature decreases. Thus, for example, the percent of dissolution of CaO at 10°C is 1.5 times higher than at 70°C.

TABLE 3.1. CHANGE IN CEMENT SETTING TIMES DEPENDING ON TEMPERATURE

Temperature °C	Grade 300 portland cement		Grade 400 portland cement		Grade 300 Pozzuolanic portland cement		Grade 250 slag portland cement		Grade 500 bauxite cement	
	Setting times, hours-minutes									
	Start	Finish	Start	Finish	Start	Finish	Start	Finish	Start	Finish
70	0—40	0—55	—	—	0—40	0—55	1—05	1—45	—	—
50	1—00	2—00	1—30	3—00	0—45	2—10	1—45	2—45	0—30	3—10
30	1—45	2—45	1—50	4—20	1—45	4—30	2—15	5—40	1—10	4—40
15	1—05	1—45	1—45	2—45	2—15	5—40	3—55	10—45	3—30	9—30
5	4—45	14—40	9—10	18—40	6—50	16—20	5—20	23—15	4—15	21—00
0	8—00	25—35	—	—	9—50	25—25	7—35	37—25	—	—

At sub-zero temperatures cement paste usually does not set; even at  $-1$  or  $-2^{\circ}\text{C}$  the samples freeze. When the samples thaw, the cement paste sets very intensively. A similar picture is observed in studying the hardening of mortars and concretes. After thawing the rate at which their strength increases also increases. When cement paste freezes, besides temporarily stopping the cement hardening and setting process, the structure of the samples is disrupted. Subsequently temporary freezing of a cement paste has no effect on hydration ability. Therefore if necessary, when thawing freshly frozen samples, if the moisture has not been frozen, solidity may be restored and the standard strength of the cement stone ensured by vibration (see Chapter 6).

Cement setting times and intensity of heat liberation associated with them may be controlled in the necessary direction by changing the temperature of the hardening concrete or mortar.

In order not to destroy the pourability of concrete or mortar mixtures, setting of the cement should begin after placement of them in the structure has been completed. This is of interest when heating materials and when working in regions with a dry, hot climate as well as when using quick setting cement.

#### The Effect of Water-Cement Ratio on Cement Setting Times.

The results of setting tests of standard-thickness cement paste cannot be directly used with regard to concretes and mortars. The water-cement ratio is usually assumed to be within 0.4-0.8 to attain a pourable concrete mixture. Thus, the water-cement ratio of standard thickness paste is 2-3 times less than the water-cement ratio in concretes. Therefore, in order for the laboratory test to approximate industrial conditions three typical cements were tested not only in a paste of standard consistency, but also with a  $W/C = 0.4$  and  $0.5$ . In doing this the excess water in the paste with the increased  $W/C$  separated above, as the result of which noticeable slumping of the paste occurred in the rings.

The cement setting times were determined at 5, 15 and  $30^{\circ}\text{C}$ , and for portland cement at 0 and  $50^{\circ}\text{C}$  as well. Before mixing the cement paste the temperature of the cement and water were brought to that established according to the experimental conditions. The cement paste was mixed and placed in the rings at normal temperature, and then the samples were transferred to cabinets with the appropriate temperatures. The results of the tests are cited in Table 3.2.

It is apparent from the data that as the water-cement ratio increases the start and finish of setting diverge. The start of setting of the paste at a  $W/C = 0.4$  is 2-3 slower than a paste of normal thickness. At high temperatures the start of setting of the cement paste of very loose consistency begins at times quite suitable for practical purposes. In these cases the time between the start of cement setting and its finish is considerably less than at normal temperature.

TABLE 3.2. CEMENT SETTING TIMES AT VARIOUS WATER-CEMENT RATIOS AND TEMPERATURES

Temp. °C	W/C=0.27		W/C=0.3		W/C=0.5	
	Setting times, hours-minutes					
	Start	Finish	Start	Finish	Start	Finish
Grade 300 portland cement						
30	2-20	3-40	4-20	5-40	4-00	5-40
15	4-00	5-25	8-10	10-00	9-00	10-15
5	4-45	10-20	12-20	21-00	17-10	25-10
Grade 250 slag portland cement						
50	1-45	2-45	2-45	3-30	3-15	4-05
30	2-15	5-40	5-40	9-10	7-05	11-20
15	4-00	13-05	11-40	21-40	13-10	25-20
5	5-20	23-15	14-30	30-45	19-00	40-35
0	7-45	37-25	22-25	51-15	28-30	59-25
Grade 500 bauxite cement						
30	1-45	4-25	4-00	7-50	7-10	8-10
15	2-20	9-45	14-00	15-00	15-00	16-00
5	5-10	10-00	—	—	—	—

This may be explained by the fact that initially the cement particles are dissociated in a large amount of water, and the new formations do not reach the necessary concentration. Then, on the one hand, the water separates upwards and the cement particles settle downward (with unavoidable thickening of the paste under its own weight), on the other hand, as the W/C increases, the calcium hydrosilicate gel forms more intensely as do the crystals of the calcium hydroaluminates and calcium hydroxides which, although later, still rapidly form the structure of the cement stone. The paste begins to lose plasticity more rapidly and the cement completely sets. It is shown in Figure 3.1 to what degree the change in the temperature and the water-cement ratio affect the change in the cement setting rates.

It is apparent from the results obtained that the increased water-cement ratio, as well as the lowered temperature, by a factor which retards the formation of the gel structure with crystalline concretions and thus a factor which retards the cement setting times. Thus, an increase in mobility of the concrete mixture lengthens the time during which it can be placed in the structure.

However, this method of lengthening the placement time of a concrete mixture leads to a drop in the concrete strength and can be used only if absolutely necessary.



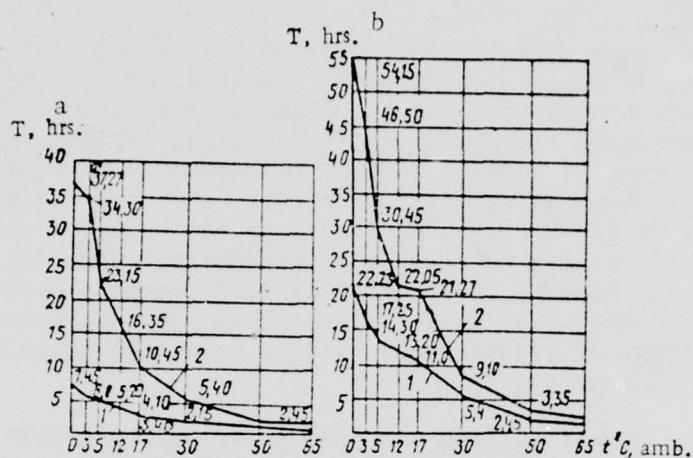


Figure 3.1. Effect of Temperature and W/C on the Setting Times of Type 250 Slag Portland Cement. a, Cement paste of normal thickness (W/C = 0.27); b, Cement paste at W/C = 0.4; 1, Start of setting; 2, Finish of setting. Commas indicate decimal points.

#### Admixtures-Cement Setting Time Accelerators.

It has been established that calcium chloride is the best additive in the capacity of an accelerator of cement hardening and setting times.

The characteristics of the setting times of four cements tested in a standard procedure, but at 5, 15 and 30°C with and without the addition of 2% calcium chloride (by mass of the cement) are shown in Table 3.3.

Tests have shown that the greatest acceleration of setting times with added calcium chloride occurs when using bauxite cement.

Portland cements of varied mineralogical composition with the same addition of calcium chloride also have different setting times. In all cases the greatest effect in accelerating the setting time is attained at reduced above-zero temperatures.

Many tests have shown that when 1%  $\text{CaCl}_2$  is added portland cements under normal conditions set on the average 1.5 times faster, and when 2%  $\text{CaCl}_2$  is added 2.5 times faster than when the additive is not used. With smaller additions of calcium chloride (1-1.5%) pozzuolanic portland cements shorten setting times to a lesser degree than portland cements.

Sulfuric and hydrochloric acids which form during the hardening process of gypsums and calcium chloride may be used to accelerate cement setting times. Other chemical additives, accelerators of cement setting and hardening times, usually result in the concretes and mortars losing their ultimate strength, and therefore as a rule, are not recommended for use.

In individual cases a mixture of portland cement and bauxite cement can be used instead of chemical additives to accelerate setting times. Based on work experience in building the Chusovskiy Factory, 5% bauxite cement may be recommended as an additive to portland cement. When more than 10% bauxite cement is added, the portland cement sets almost instantly and an experimental check is necessary for this. For these same purposes 5% portland cement or fresh non-carbonized lime can be added to bauxite cement. These additives may be especially appropriate under fall-spring conditions and at the casting yards of reinforced concrete constructions. Finally, it must be noted that an increase in the grinding fineness without supplementary addition of gypsum leads also to an acceleration of the setting times of all cements.

TABLE 3.3. CEMENT SETTING TIMES AT 5, 15 AND 30°C WITH 2% CALCIUM CHLORIDE ADDED

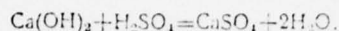
Cement	Standard thickness, %	Temperature, °C					
		5		15		30	
		Setting times, hours-minutes					
		Start	Finish	Start	Finish	Start	Finish
Grade 400 portland cement from the "Red October" Factory	27.75	9-10	18-40	3-30	7-25	1-55	4-25
The same, with 2% CaCl <sub>2</sub> added	27.75	4-15	8-50	3-00	4-40	1-00	2-25
Type 400 portland cement from the Kramatorskiy Factory	25	7-50	15-05	5-30	8-15	1-50	4-05
The same, with 2% CaCl <sub>2</sub> added	25	0-30	2-00	1-50	3-05	1-15	1-50
Grade 500 bauxite cement	26.25	4-15	24-00	3-30	9-30	1-10	4-40
The same, with 2% CaCl <sub>2</sub> added	26.25	-	-	0-20	0-30	0-10	0-40

#### Admixtures-Retarders of Cement Setting Times.

In factory production of quick setting cements (for example, without additive or in a case of insufficient addition of gypsum during the clinker grinding) it becomes necessary to take measures to retard their setting times.

The gypsum available at the site should be, as a rule, first mixed with cement.

When gypsum is not available at the site, it may be replaced by a small amount of added sulfuric acid. In this case  $\text{Ca(OH)}_2$  interacts with sulfuric acid  $\text{H}_2\text{SO}_4$  and forms calcium sulfate in accordance with the following replacement reaction:



Consequently, the addition of sulfuric acid leads to the formation of a di-hydrous gypsum which is very highly dispersed; this exerts a greater effect than the addition of gypsum.

At normal temperature the addition of 0.25% sulfuric acid by mass of mixture water delayed the start of setting of non-gypsum slag portland cement from 4-7 minutes to 1 hour 15 minutes in our experiments, and when the outside temperature was reduced to 3°C to 4 hours 10 minutes.

In 1942-1943 at the site of the metallurgical factory in Zlatousto, the setting times of non-gypsum cement were reduced by adding water containing sulfuric acid wastes to the concrete. During the Great Patriotic War, when some factories produced cements without gypsum added as a regulator of setting times, it became necessary to develop measures for using these cements in construction. In winter and fall-spring we solved this problem rather simply by using a reduced temperature of the medium (5-10°) and an increase as an exception of the workability of the concrete mixture (slump approximately 8-10 cm). At the factory site in Chebarkul these measures made it possible to pour the cement mixture with a small over-consumption of cement in 30-45 minutes using "bystryak" [quick] cement with a total setting time of 4-7 minutes.

Cement setting times can also be delayed by adding not more than 1.5% of the cement mass phosphoric acid. When phosphoric acid is added, the concrete mixture solidifies very slowly; this makes it possible to delay the placement and consolidation times of the concrete in the structures by 10-15 hours. In some cases, in particular during long interruptions in concreting, this is necessary.

When small fractions of a percent of workability agents and sugar substances are added to a concrete mixture the setting and hardening times are also considerably retarded.

In accordance with construction requirements we can now control (change in a directed manner) cement setting times by creating certain temperature conditions and by introducing various additives.

#### Plastic Strength and Certain Physical Characteristics of Cement Paste.

Together with setting times let us examine such characteristics as plastic strength, heat liberation, the change in alkali content, electrical conductivity, the contraction phenomenon and their interrelationship in the setting of a cement paste. In our studies it was established that the true finish of cement setting is not sufficiently determined using a Vicat apparatus.

According to the indicators of heat liberation, electrical resistance, contraction, and the change in alkali concentration in the liquid phase (according to CaO) the finish of cement setting begins somewhat later than is established by the Vicat apparatus. A systematic model of the



interrelationship between the saturation of the liquid phase with calcium hydroxide, the increase in temperature, the change in electrical resistance and the increase of plastic strength of a cement paste in comparison with standard cement setting time is shown in Figure 3.2.

As is apparent from the figure, the salient points on the curves of temperature, electrical resistance and plastic strength correspond to the maximum saturation of the liquid phase with CaO. The end of the setting period characterizes the process of structure formation and the beginning of intense hardening of the cement.

In work [3] the plastic strength was determined with a conical plastometer. The study was conducted on 3 cements whose setting times are shown in Table 3.4.

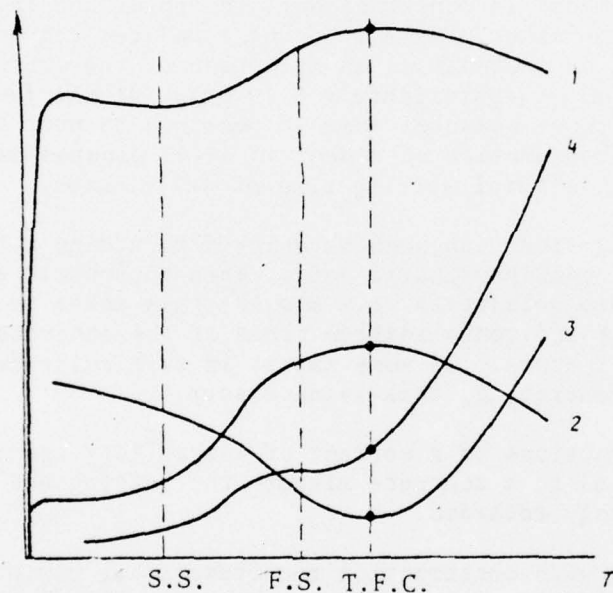


Figure 3.2. Changes in Cement Paste in the Initial Hardening Period. 1, CaO concentrations in the liquid phase; 2, Heat liberation; 3, Electrical resistance; 4, Increase in plastic strength; S.S., Start of setting; F.S., Finish of setting; T.F.S., True finish of setting.

TABLE 3.4. SETTING TIMES OF CEMENT PASTE IN ACCORDANCE WITH GOST 310-60

Portland cement	Setting times, hours-minutes	
	Start	Finish
Belgorodskiy	3-28	5-43
Voskresenskiy	1-06	4-40
Nevyanskiy	2-20	3-45

The plastometer cone was immersed into the cement paste at a constant depth of 5 mm measured with a dial gauge. Measurements were taken every 15 minutes up to the moment the cement paste hardened.

The plastic strength is calculated according to the formula

$$P_m = K_\alpha \frac{F}{h_m^2},$$

where  $F$  - load on the cone; kg;

$h_m^2$  - depth of immersion of the cone, cm;

$K_\alpha$  - constant of the cone determined according to the formula

$$K_\alpha = \frac{1}{\pi} \cos \alpha \cot \alpha.$$

Figure 3.3 shows the curves of the change in plastic strength of a cement paste of normal thickness mixed using Belgorod, Voskresenskiy and Nevyanskiy portland cements. As is apparent from the figure, soon after mixing the Belgorod and Nevyanskiy cements with water, a small increase in the plastic strength and some growth of it with time are observed. The strength increases sharply beginning approximately from 3 hours 15 minutes for Belgorod and with 1.5 hours with Nevyanskiy cement. This considerable increase in the strength is caused by the development of a crystallized structure. The curves in Figure 3.3 show a more rapid development of the process of structural formation for the Voskresenskiy cement compared to the Belgorod and Nevyanskiy cements; this may be explained by the addition of tripoli in the Voskresenskiy cement which considerably increases its structural viscosity. We may note that the greatest increase in the plastic strength is observed in the period corresponding in time with the start of setting of the cement paste determined using the Vicat apparatus. The effect of contraction of the system develops most intensively in this period (Figure 3.4).

The process of structural formation of the cement stone can also be traced from the heat liberation curves. Heat liberation is the result of the binder hydration process and gives some idea about the structural formation of the cement stone. The first period is characterized by low heat liberation which begins immediately after mixing the cement with water. Then (approximately 3 hours) the induction period occurs in which no increase in heat liberation is observed, since the cement grains are covered with a film of the gel-like hydration products which retards the hydration process. Beginning from 3 hours (the start of setting according to the Vicat device for Belgorod cement), an insignificant, and after 5-6 hours a more noticeable increase in the temperature of the cement paste takes place. Similar curves are obtained for Voskresenskiy and Neviyanskiy cements, in which a noticeable increase in the temperature of the cement paste also occurs after 5 hours.

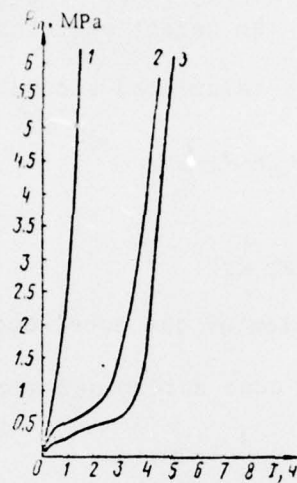


Figure 3.3. Change in the Plastic Strength of Cement Paste of Normal Thickness at  $t = 20^{\circ}\text{C}$  Mixed Using Portland Cements. 1, Voskresenskiy; 2, Nevyanskiy; 3, Belgorod.

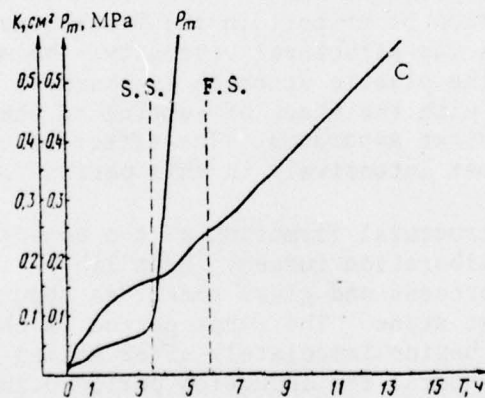


Figure 3.4. Change in the Plastic Strength (P), Contraction (C), the Start (S.S.) and the Finish (F.S.) of the Setting Times of a Cement Paste of Normal Thickness Containing Belgorod Portland Cement at  $t = 20^{\circ}\text{C}$ .



The changes which occur in a cement paste and concrete during their hardening cause a change in their electrical physical characteristics. Therefore some researchers [10, 45, 74] monitor the setting and hardening process of cement from the change in its electrical conductivity, dielectric permeability, the tangent of the angle of dielectric losses. Each stage in concrete hardening is matched by its own electrophysical characteristics. Thus, a qualitative characteristic of the physical-chemical processes taking place in the early stage of hardening may be obtained from the change in electrical conductivity. The finish of setting corresponds to a sharp increase in electrical resistance (or to a drop in electrical conductivity). The ohmic resistance which must be known in the electrode method of concrete electrical thermal treatment depends primarily on the moisture content and the specific resistance of the liquid phase saturated with alkalis and mineral salts. As the temperature increases the specific resistance of the mixture drops, and it rises during the hydration (binding of part of the water) and hardening process of the cement. Introduction of chemical additives, electrolytes, into the cement paste or the concrete causes an increase in electrical conductivity. The specific electrical resistance of a cement paste is not a constant, but changes as it hardens. Below 0°C the amount of liquid phase in the cement paste drops, and the content of solid (ice) phase increases. In this case the electrical conductivity of the cement paste or hardening cement stone (concrete) drops sharply.

The effect of early freezing of cement paste on the hardening processes in the initial stage as well as after thawing have been studied in works [2, 21] on the kinetics of electrical conductivity of test samples (Figure 3.5). It has been established that the maximum electrical conductivity of cement paste after thawing ( $\gamma_{\max}^{\text{A.T.}}$ ) differs from its value at the instant freezing begins ( $\gamma_0$ ). It is considerably lower than the initial value and lower than in test samples not exposed to freezing.

It must be emphasized that all these physical characteristics are auxiliary to the standard method of testing cement paste. They are used primarily in scientific-research works. The attempt by L. A. Silchenko and M. V. Mithalov to establish the optimum start times for thermal treatment from a plastogram curve of cement paste yielded unsatisfactory results. On the basis of the salient points obtained on the plastograms, they recommended to certain Moscow precast reinforced concrete factories that the preliminary curing times of articles before the beginning of thermal treatment be reduced 0.5-1 hour. Their statements that concrete strength increases 25-35% by reducing the curing times of parts before steaming were not confirmed in practice. This example points up the necessity of a complex examination of the phenomena and parameters which characterize the properties of cement and concrete. It is impossible to use mechanically the individual characteristics of hardening cement when solving problems in concrete technology under factory as well as construction conditions. A broad scientific approach to this problem which covers all aspects of the phenomena is required at the contemporary level of development of concrete theory and technology.

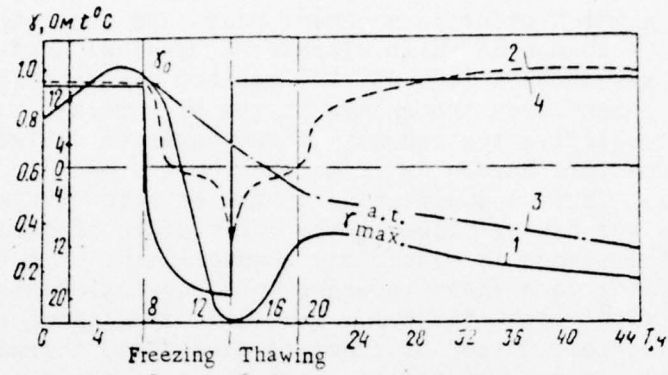


Figure 3.5. Change in the Properties of Cement Stone During Freezing, Thawing and Subsequent Hardening. 1, Electrical conductivity of the cement stone; 2, Temperature of the cement stone; 3, Electrical conductivity of the test sample; 4, Ambient temperature.

#### CHAPTER 4

### EFFECT OF THE TEMPERATURE OF A CONCRETE MIXTURE ON ITS CONSISTENCY AND THE CONCRETE STRENGTH

During concrete and reinforced concrete operations the consistency of the concrete mixture which depends on the amount of cement paste, additive content, curing time before placement, type of coarse and fine aggregate, their ratio in the concrete and other factors is of considerable importance.

The author conducted tests on 4 different types of cements to determine certain dependencies. The workability of the concrete mixture in the initial period was characterized by a slump of 3 and 9 cm, the consumption of portland cement was  $270 \text{ kg/m}^3$ , bauxite cement  $236 \text{ kg/m}^3$  and sand-pozzuolanic portland cement  $303 \text{ kg/m}^3$ . The materials were pre-heated to ensure a temperature of 20, 30 and  $40^\circ\text{C}$  of the concrete mixture. The concrete was mixed with an additive of 1-3% calcium chloride (of the cement mass) and without additives. The concrete mixture was cured at the site at an air temperature of  $15\text{-}20^\circ\text{C}$ .

The changes in the consistency of the cement mixture from slump and its pourability measured using an industrial viscosimeter are shown in Figure 4.1. The consistency of the prepared mixture was determined first, and then its pourability in seconds using the industrial viscosimeter. At a mixture temperature of  $30\text{-}40^\circ\text{C}$  it loses workability more rapidly than at  $20^\circ\text{C}$ .

In Figure 4.1 the drop in mixture workability is shown by solid lines, the drop in pourability by dotted lines. The measurements were taken during the times indicated on the figure.

As tests have shown, as the temperature increases the workability of the concrete mixture drops in all cements. Addition of 1-2% calcium chloride at the same temperature does not lead to any significant changes (as the result of the increase in workability of the mixture due to the additive itself), and when 3% is added workability and pourability drop noticeably. With still larger additions of salts the water requirement of the cement mixture decreases, and the loss of pourability accelerates.

Concrete mixed using sand-pozzuolanic portland cement loses workability and pourability much more rapidly than mixtures using portland cements. In this cement the pourability of the mixture is generally reduced. The addition of calcium chloride when using pozzuolanic portland cement results in an increase in the workability of the mixture.

The loss of workability and pourability of a concrete mixture is related in a certain way to cement setting. The addition of calcium chloride reduces the setting times of bauxite cement and portland cement. Concrete containing bauxite cement with added calcium chloride loses workability even more quickly than that containing portland cement.



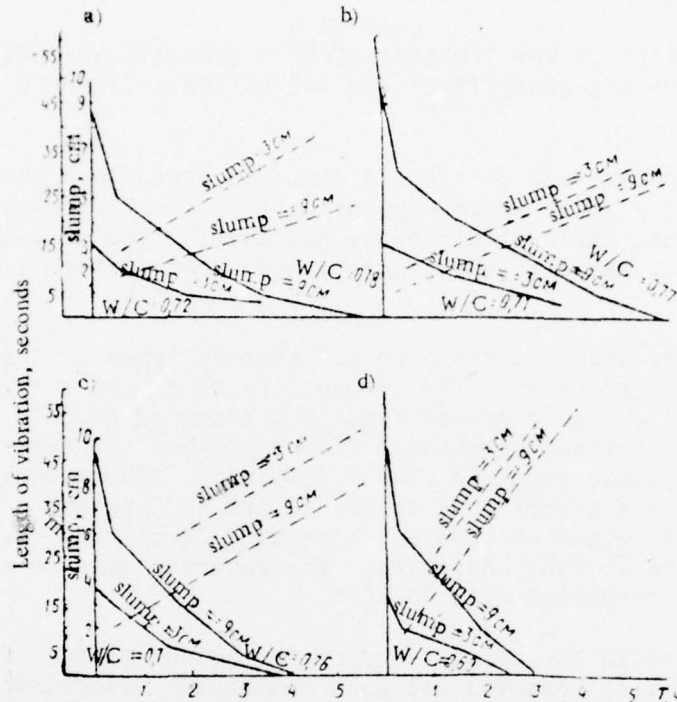


Figure 4.1. Change in the Workability and Pourability of Concrete Mixed Using Grade 400 Portland Cement Depending on Curing Time at  $t = 20^{\circ}\text{C}$ . a, Without  $\text{CaCl}_2$  added; b, With 1%  $\text{CaCl}_2$  added; c, With 2%  $\text{CaCl}_2$  added; d, With 3%  $\text{CaCl}_2$  added.

The effect of preliminary curing of the mixture before placement on the concrete strength was studied at the same time the pourability of concrete mixtures was determined. The concrete samples were prepared on the vibration platform, the mixture was placed immediately after mixing and approximately 5 hours 30 minutes later. The concrete mixture was characterized by a slump of from 3 to 6 cm. Data about the strength of the concrete after 30 days of normal hardening are cited in Table 4.1. In all cases the mixture consolidated well and the consolidation time rose as the amount of preliminary curing increased.

TABLE 4.1. EFFECT OF CURING TIME OF A CONCRETE MIXTURE WITH AND WITHOUT CALCIUM CHLORIDE ADDED ON THE STRENGTH OF THE CONCRETE AT AGE 30 DAYS

Cement	Cement consumption, kg per 1 m <sup>3</sup> of concrete	W/C	Concrete compress. strength limit, MPa, when placing mixture in form							
			Immed. after preparation		After					
			Without CaCl <sub>2</sub>	With 2% CaCl <sub>2</sub>	2 hours		4 hours		5 hours 30 min.	
			Without CaCl <sub>2</sub>	With 2% CaCl <sub>2</sub>	Without CaCl <sub>2</sub>	With 2% CaCl <sub>2</sub>	Without CaCl <sub>2</sub>	With 2% CaCl <sub>2</sub>	Without CaCl <sub>2</sub>	With 2% CaCl <sub>2</sub>
Start of mixture placement			30 minutes		2 hours		4 hours			
Grade 500 bauxite cement	230	0,78	35,1	27,2	35,1	28,6	34,7	27,4	42,4	36,8
Grade 400 portland cement	276	0,68	11,7	14,8	12,7	18	13,7	18,2	15,3	18,5
Grade 400 portland cement	275	0,7	11,5	12,5	13,5	12,1	13,9	14	13,9	17
Start of mixture placement			1 hour		2 hours		3 hours			
Grade 300 sand-Pozzuolanic portland cement	305	0,68	9,7	13,2	10,6	13,4	11,3	15,4	11,6	16,6

Notes: 1. The cements began to set within 2 hours 10 minutes-4 hours 5 minutes, and setting ended within 5 hours 30 minutes-7 hours 50 minutes.

2. If the mixture was placed at a time different from that shown in the appropriate column, the new time for the individual components is indicated above the figures for sample strength.

Commas indicate decimal points.

As can be seen from Table 4.1 3-5.5 hour curing of the prepared concrete containing all 4 cements led to an increase in the concrete strength. With the indicated workability of the concrete mixture the addition of 2% calcium chloride did not prevent placement of the concrete in the forms before 3-5.5 hours. Analysis at age 30 days showed a considerable increase in the strength of the concrete containing all cements except for the bauxite cement. Preliminary curing of the mixture before placement for 5 hours 30 minutes increased the strength of concrete mixed using portland cements without CaCl<sub>2</sub> added by 20 and 30%, and that containing bauxite cement by 21% of its graded strength after 4 hours of curing. At the time these tests made it possible for the author to suggest the feasibility of utilizing preliminary curing of concrete mixtures before placement.

Further tests showed that the greatest increase in strength is attained when the mixtures are cured at reduced above zero temperatures and especially before beginning thermal treatment of the parts or cast in situ structures. This is in good agreement with recommendations for repeated vibration in general and with the suggestions stated in Chapter 6 about concrete vibration at the instant of thawing if it had been frozen immediately after preparing the mixture.

Concretes mixed at low above-zero temperatures may provide a significant saving in cement. The increase in the concrete strength, and consequently the possible saving of cement, are achieved firstly due to the smaller water requirement of the mixture, secondly due to the absence of irreversible thermal expansion of the concrete at higher temperatures.

The problem of increasing concrete strength should be regarded in direct relation with saving cement. This conclusion should be considered when establishing cement consumption standards for cast in situ concrete, including during winter concreting and during concreting under dry and hot climatic conditions. Previously these questions had not been raised to the level of cement consumption standardization depending on the temperature at which the mixtures were prepared and placed. In spite of favorable temperature conditions for preparing the mixtures and hardening the concrete in structures, frequently in winter builders attempted to increase cement consumption compared to ordinary consumption during the warm part of the year. A different picture is obtained when placing concrete mixtures under dry and hot climatic conditions. Set grades of concrete cannot be attained there during summer months without additional cement consumption, and the quality of not only cast in situ structures, but prefabricated parts will not meet the requirements of standards and norms. Therefore it is necessary to develop special measures for mixing and curing concrete at reduced as well as the most favorable temperatures.

Many tests have shown that the rheology of concrete mixtures depends largely on temperature. Therefore during winter concreting the preheating of materials or warming-up of prepared concrete mixtures using any method should always be examined in conjunction with their placeability and with the strengthening of the concrete during subsequent hardening.

In past years the mixing and supply of mixtures with an increased temperature (30-40°C) from cement factories were conducted mainly by preheating the aggregate and water. Recently efficient methods of preheating concrete mixtures such as electrical heating in bunkers and steam heating in concrete mixtures have been developed. At present, for example, steam heating of concrete mixtures in concrete mixers is used in precast reinforced concrete factories and commercial concrete factories in Denmark, the FRG, the GDR, Poland and other countries. Closed forced action concrete mixers are mainly used for this purpose. Experience shows that in them a mixture can be heated to a temperature of 60-80°C for 3-5 minutes. The mixture heats up more uniformly than during electrical heating, in which considerable temperature gradients occur horizontally in the bunker as the result of the unequal electrical conductivity of the mixture. To achieve uniform preheating of mixtures with an electrical current it is necessary to determine the electrode structure and change their surface for the height of the bunker.

Electrical preheating was very efficient at construction sites where the mixtures are placed directly in the formwork. The disadvantage of using an electrical current to preheat the mixture at the factories lies in the temporary requirement for high power transformers.



Just as preheating of materials, steam preheating of a concrete mixture in a concrete mixer and electrical preheating of it have a considerable effect on the consistency of the mixture and the strength of the concrete since they cause the mixture to thicken and lead to an increased water requirement. Although as the temperature increases the viscosity of the mixing water drops, accelerated development of cement setting and hydration processes leads, however, to thickening of the mixtures and make them difficult to place.

The effect of the temperature factor on the consistency of a concrete mixture and concrete strength was studied as early as the 1930's [9]. It was shown in this work that preheating of materials changes the consistency of the concrete mixture only by changing the consistency of the cement paste. On the basis of experiments conducted by B. G. Skramtayev and I. A. Falkov, the authors of this work noted: "Since the consistency of a concrete selected in accordance with operating conditions and the nature of the structure to be concreted cannot be significantly changed without damaging the course of concreting, when changing to a concrete mixture with an increased temperature the builder is faced with the additional problem of selecting a concrete composition with the same consistency when the mixture is preheated as under normal conditions.

The required consistency can be restored either by increasing the water-cement ratio (W/C) or by increasing the content of cement paste while maintaining the W/C stipulated by the established strength of the concrete constant, i.e., when increasing cement consumption. Tests show that if it is decided to increase the W/C, it will cause a 20-30% drop in the strength of the concrete. Since such a drop in strength is not permissible, it is possible to change to an increased W/C by replacing grade 0 cement with higher grades of cements of grades 00 and 000 at the same time.

When the mixture temperatures are raised the consistency of the concrete can be maintained, as has already been pointed out, by increasing cement consumption (while simultaneously maintaining the set W/C) by approximately 15-20%.

At one time, I. A. Kireyenko conducted studies on the question of the effect of cement paste temperature on its consistency and showed that as the temperature of the paste increases the amount of water necessary to produce its standard thickness increases; this leads to an increase in the amount of mixing water. Accordingly this dependency is applicable to the mixing of concretes with increased temperatures.

Unfortunately, the starting precepts of concrete technology indicated above concerning the effect of the temperature factor on the consistency of concrete mixtures and concrete strength which were developed by many scientists in the thirties are occasionally ignored at the present time when developing new technical methods of raising the temperature of concrete mixtures before placement. Of course this leads to serious errors on the part of a number of researchers who evaluate the advantages of some method of preheating concrete mixtures.

In the Recommendations of the All Union Scientific Research Institute of Industrial Technology of Precast Reinforced Concrete Structural Parts and Products, 1972 edition, it is pointed out that the consistency of a preheated concrete mixture at the moment it is placed is ensured by increasing the water consumption by 5-25% vis-a-vis water consumption for a mixture placed in the cold state. The increase in water consumption depends on the type of cement used, type of concrete, preheating temperature conditions, additives used and other factors. The data of the Recommendations as well as many other publications do not point out the corresponding increase in cement consumption.

Few authors and industrial documents point out the necessity of increasing cement consumption to maintain the accepted water-cement ratio when preheating a concrete mixture. The same can be said about steam heating concrete mixtures in concrete mixers.

Recently the question of the effect of the temperature factor on the consistency of a concrete mixture and concrete strength has become very important for concreting operations under hot, dry climatic conditions. As is generally known, one of the most important problems of concreting under these conditions is the maintenance of the required concrete mixture consistency when placing it. In this case principal attention is devoted, as a rule, to questions of maintaining the workability and homogeneity of the mixture when transporting it to the concreting objectives or during preplacement curing under increased temperature conditions. Considerably less attention is devoted to the question of ensuring the supply workability of a concrete mixture with an increased temperature. At the same time there exists an inversely proportional dependency between the temperature of the concrete mixture and its workability which is noted in some data in the literature and which has been confirmed by research conducted in the cement hardening acceleration laboratory of the Scientific Research Institute of Concrete and Reinforced Concrete.

Under summer conditions in regions with a hot climate the temperature of the concrete mixture is approximately 30°C when it is taken from the concrete mixer, sometimes increasing to 35°C and even more. At these temperatures a mixture of the same composition is considerably less workable than at normal temperatures.

In conjunction with new technological decisions in winter concreting as well as that under hot and dry climatic conditions the author along with Ye. M. Malinskiy, Ye. S. Temkin, O. A. Samusev and A. M. Nevakshonov are conducting laboratory and full-scale studies at building projects in Tashkent and Bukhara.

Recommendations for hot weather concreting were published in 1972 in the U.S.A. It is pointed out in these recommendations that a 10-12°C increase in the temperature of freshly mixed concrete leads to a 2.5 cm reduction in its initial slump (Figure 4.2). The water requirement of concrete mixtures changes in the following manner as the temperature increases.

Temperature of the concrete mixture, °C	5	10	15	20	25	30	35	40
Amount of water per 1 m <sup>3</sup> of concrete, kg	157	160	163	167	170	173	177	180

These data are cited without consideration of concrete content, the water-cement ratio, the workability of the concrete mixture, the type of cement and aggregate used, and other technological factors which significantly affect the initial workability of the concrete mixture depending on its temperature.

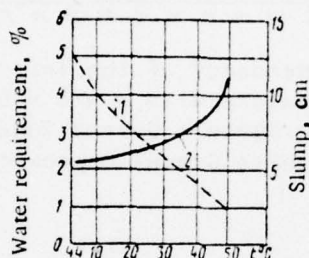


Figure 4.2. Effect of Concrete Temperature on Slump and the Amount of Water Required to Change It (Cement Content 307 kg/m<sup>3</sup>, Aggregate Size Approximately 3.8 cm). 1, Slump; 2, Water requirement.

Special studies were conducted by the author and Ye. N. Malinskiy (Scientific Research Institute of Concrete and Reinforced Concrete) to establish the effect of these factors on the nature of the dependency of slump on the temperature of the concrete mixture. The dependency between the temperature of the various concrete mixtures and their initial workability for concretes mixed using grade 400 Belgorod portland cement is cited in Figure 4.3 as an example.

Studies conducted on cements of varying mineralogical content and varying grinding fineness as well as on concretes of various compositions showed that the initial workability of the same mixture at  $t = 20^{\circ}\text{C}$  (for which cement consumption standards are usually established) and at  $t = 30^{\circ}\text{C}$  differs more the lower the W/C. To establish this difference it is necessary to increase water consumption and accordingly cement with the W/C the same in preparing a mixture with a temperature of  $30^{\circ}\text{C}$ . The studies which have been conducted have made it possible to establish the dependency of water (and cement) consumption on temperature of the concrete mixture to obtain compositions of equal workability (and equal strength). Figure 4.4 shows this dependency in graph form.

Studies have demonstrated the significant effect of the W/C and some effect of the consistency of a concrete mixture on the nature of its change depending on temperature.



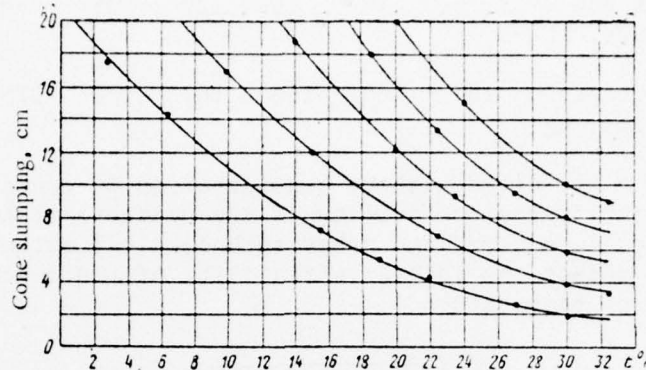


Figure 4.3. Dependency of the Initial Workability of a Concrete Mixture with a W/C = 0.45 on its Temperature (Aggregate - Quartz Sand with  $M_{size} = 2.4$ , Granite Gravel Approximately 5-30 mm).

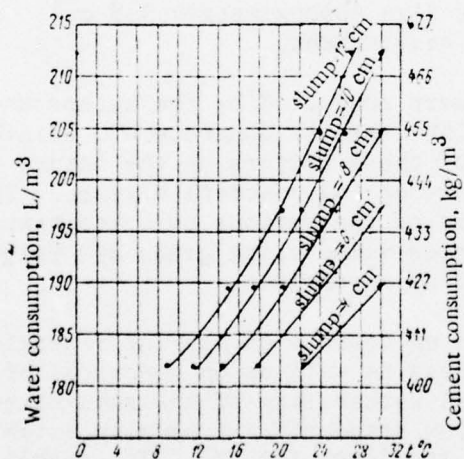


Figure 4.4. Water and Cement Consumption as a Function of the Change in Temperature of Concrete Mixtures of Varying Workability. Concrete mixed using portland cement at a W/C = 0.45.

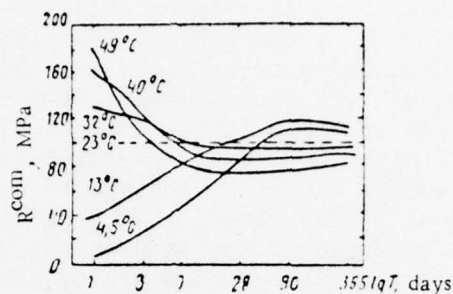


Figure 4.5. Effect of Temperature on Concrete Compression Strength (According to P. Kliger).

As we have already pointed out, the increase in cement consumption in mixing concrete with an increased temperature and the decrease of it when producing mixtures with a reduced temperature are not stipulated by existing standards. At the same time, as follows from Figure 4.4, when the concrete mixture temperature drops below 20°C water consumption (and consequently cement as well) may be considerably decreased to produce mixtures of equal workability (and equal strength). It is clear that when considering this situation in mixing concrete in winter (without first preheating it) cement can be saved in many cases. To avoid using too much cement during concreting operations at an increased temperature it is necessary to use different additions of surface active substances and other technological measures. Surface active additives promote the conservation of mixture consistency during transport to the placement location.

In conjunction with the dependencies under examination of water and cement consumption at different temperatures of the concrete mixtures, the results of studies of P. Kliger (U.S.A.) on establishing the relationship between concrete strength and temperature of concretes containing portland cements are cited in Figure 4.5. The concrete strength was tested not only at age 1 month, but after even longer periods of time.

Concretes of equal strength designed to reach rated strength by age 28 days subsequently became stronger the lower the temperature of the concrete mixture during placement.

TABLE 4.2. COMPRESSION STRENGTH OF SAMPLES, MPa

Hardening conditions of portland cement samples after initial mixing	Average strength of the 6 samples		Total strength for both tests
	After initial mixing	After repeated mixing	
In water at a temperature: 3°C (in a refrigerator)	49,7	25,8	75,5
18°C	58	16,8	74,8
45°C (on a thermostat)	65	9,6	74,6

Commas indicate decimal points.

In conjunction with this it is also interesting to cite the results of a single experiment performed by the author. Samples of cement paste of normal thickness were cured in water at 3, 18 and 45°C for 28 days, then pulverized to the fineness of ground cement after the strength test and again mixed. The results of these tests (Table 4.2) showed that after the initial mixing and hardening the cement was still rather highly active due to the unhydrated portion of it which remained in the grain nucleus. In this case the greater mass of the cement grains was hydrated after the initial mixing (the higher strength of the samples was the criterion for this), the less was hydrated after the second mixing (the lower strength of the samples was the criterion for this). The sums of the strength for both mixings under each of 3 accepted temperature conditions of curing were identical.

After the second mixing all the samples were stored in water at 18°C. The length of curing in water in the first and in the second cases was 28 days, i.e., the cement samples hardened 56 days overall.

Samples hardened first at 3°C on the whole became stronger than at 45°C. It must be assumed that subsequently this difference in strength would increase even more.

In conclusion we may state that temperature exerts a great effect on the properties of a concrete mixture as well as on the strength characteristics of concrete mixed at various temperatures.

The conclusions examined previously extend to diverse climatic conditions and relate to the production of cast in situ reinforced concrete as well as concrete and reinforced concrete parts under factory conditions to a varying degree.



CHAPTER 5  
HARDENING AND PROPERTIES OF CONCRETE CONTAINING  
VARIOUS CEMENTS AND AGGREGATES DEPENDING ON TEMPERATURE

Hardening of Concrete Containing Different Cements Under Normal Conditions.

The rate of strengthening and final strength of concrete depends on many factors. The principle of these are the activity of the cement and the water-cement ratio; therefore the strength of the concrete is a function primarily of these values:

$$R_{\text{con}} = f(R_{\text{cem}}, W/C).$$

Let us examine the rate of strengthening of concrete containing various types of cements and its activity under normal temperature-humidity conditions. As studies show, the same types and grades of cement frequently strengthen at a different rate during the first month and in the following period. This is explained to a large degree by the chemical-mineralogical composition of the cement clinker and the introduction of ground additives at the factories.

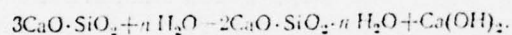
Cements with a high content of calcium aluminates are distinguished by their high rate of hardening. In this case the less basic of the calcium aluminates, the higher the strength attained when the cements harden. An increase in basicity (i.e., increase in the number of molecules of calcium oxide in the composition of the calcium aluminate mineral) leads to still greater acceleration of the setting and hardening processes of bauxite cement; however in this case it causes a sharp drop in the strength of the cement stone and consequently of the concrete due to the formation of highly basic calcium hydroaluminates.

A rapid increase in strength during the first month and the relatively lesser increase of it in the following period are noted when using portland cement with a high content of tricalcium silicate. When the content of bicalcium silicate is increased portland cement hardens slowly during the first month and its strength increases more intensively later. Thus, when the content of tricalcium silicate is increased in portland cement the strength of the concrete increases (see Figure 5.1).

The results of tests with concretes of the same composition stored under normal conditions were taken to establish this dependency, but a varying amount of  $C_3S$  was included in the cement composition (from 25 to 61.5%). As is apparent from the graph, if when maintaining 25%  $C_3S$  in the portland cement the concrete had a strength of 11 MPa at age 1 month, at 61.5%  $C_3S$  in the cement the strength of a concrete of the same composition approached 25 MPa. It is obvious that as the  $C_3S$  content in portland cement increases the grade of cement and rate of its hardening increased.

As was shown in Chapter 2, approximately 30% of the water is chemically bound and physically (by adsorption) retained when the portland cement hydration process finishes. Consequently, with ordinary W/C values above 0.3, the remaining water used to mix the concrete is necessary only because of poorly improved methods of consolidating a concrete mixture. The introduction of an excess amount of water leads to a reduction in density and strength, and consequently the durability of concrete in various media. Therefore we must attempt to reduce the amount of water added to the concrete mixture and increase the efficiency of methods of consolidating the mixture during placement.

The precipitation of free lime during hydrolysis and hydration of portland cement clinker characterizes the basicity of the calcium silicates and the degree of decomposition of the tricalcium silicate. During hydration of tricalcium silicate 2 molecules of CaO become part of the hydrosilicate and 1 molecule of CaO is precipitated in the form of free calcium oxide hydrate according to the following equation given in its general form:



Theoretical calculation according to the equation cited shows that free calcium oxide hydrate is liberated in the amount 33.5% of the mass of the hydrated tricalcium silicate. An insignificant amount of calcium hydroxide precipitates during the hydration of bicalcium silicate, and the remaining minerals of the cement clinker do not yield free lime.

In conjunction with this the type and amount of finely ground silicon additives should be selected depending on the tricalcium silicate content in the cement. The intensity of cement hydration and precipitation of free lime in doing this is accelerated as the temperature increases.

Free lime is essentially the basic cause of the deterioration of cement stone by the action of water filtering through the structure thickness as well as by the action of water containing various aggressive substances. Calcium oxide hydrate dissolves in water and is removed from concrete. This phenomenon is well known to builders from the white streaks seen on the surface of buildings in hydrotechnical and underground facilities. Moreover, when it interacts with substances dissolved in water, lime may form with the latter compounds which increase in volume or easily dissolve in water. The occurrence of formations with an increased volume in the body of cement stone leads to disruption of the concrete structure and its destruction.

Similar phenomena of dissolution and removal of calcium oxide hydrate from cement stone cannot occur in surface concrete and reinforced concrete structures. However, cement stone contains free calcium hydroxide, and if it is not necessary to bind it with pozzuolanic additives for reasons of water resistance, it is often feasible to add pozzuolana for the use of lime in hardening cement.

The rate of concrete strengthening under normal conditions up to age 180 days has been analyzed from materials of a number of researchers.

The results of the studies of V. I. Kiselev (Scientific Research Institute of Concrete and Reinforced Concrete) are of great interest; he studied the effect of the size modulus of sands on the strength of concrete made from workable and stiff mixtures of various cements. In this case the concretes were mixed with water-cement ratios of 0.4; 0.5; 0.65 and 0.8. Ordinary and plastificized grade 500 portland cements and grade 400 slag portland cement were used (from the results of tests in stiff mortars). Tests have shown (Table 5.1) that up to age 180 days the change in the size modulus of sands from 2.5 to 1.2 has no significant effect on strength or the strength increase factor of concrete with time. This relates in varying degree to concretes made from workable and stiff mixtures. The hardening intensity factor of concrete at age 7 days in concretes of workable as well as stiff mixtures increases as the water-cement ratio drops. However, in concretes of stiff mixtures the hardening intensity factors are higher than in concretes of mobile mixtures.

TABLE 5.1. CONCRETE HARDENING INTENSITY FACTORS UNDER NORMAL CONDITIONS DEPENDING ON THE CONSISTENCY OF THE MIXTURE AND THE WATER-CEMENT RATIO

Water-cement ratio	Workable mixtures			Stiff mixtures		
	$K_{7:28}$	$K_{90:28}$	$K_{180:28}$	$K_{7:28}$	$K_{90:28}$	$K_{180:28}$
Portland cement concrete						
0.8	0.62	1.35	1.38	0.7	1.3	1.33
0.65	0.61	1.21	1.24	0.72	1.2	1.41
0.5	0.76	1.24	1.28	0.75	1.23	1.26
0.4	0.76	1.13	1.22	0.86	1.14	1.21
Plastificized cement concrete						
0.8	0.57	1.56	1.59	0.64	1.41	1.78
0.65	0.63	1.53	1.63	—	1.37	1.45
0.5	0.63	1.24	1.64	0.7	1.24	1.48
0.4	0.65	1.35	1.51	0.77	1.35	1.39
Slag portland cement						
0.8	0.44	1.46	1.53	0.45	1.46	1.69
0.65	0.47	1.44	1.72	0.48	1.33	1.7
0.5	0.51	1.25	1.43	0.65	1.34	1.55
0.4	0.59	1.18	1.35	0.71	1.28	1.43

Commas indicate decimal points.



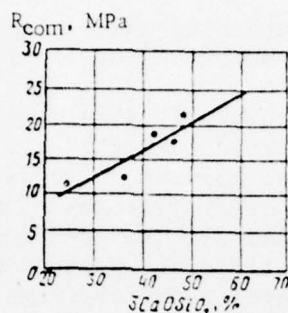


Figure 5.1. Concrete Strength at Age 28 Days as a Function of the Content of Tricalcium Silicate in Portland Cement.

At age 90 and 180 days at the same water-cement ratios the strength increase factors of concrete from mixtures of various consistency are practically the same with regard to strength ( $K_{28} = 1$ ) at age 28 days.

These factors decrease relative to the drop in the water-cement ratio. Here it should be noted that due to 40 liters less water being used per  $1 \text{ m}^3$  of concrete, and accordingly cement, the strengths of concretes of stiff mixtures were approximately 1 grade higher than in concretes made from workable mixtures. When the W/C was reduced from 0.8 to 0.4 the concrete strength at age 28 days increased at least two-fold in all cases. Consequently, the water-cement factor exerts the greatest effect on absolute strength and the intensity of its increase, especially at an early age. This is due to the fact that as the water-cement ratio decreases and the degree of stiffness of the concrete mixtures increases, the thickness of the cement glue increases.

When the concrete was mixed using plasticized portland cement, 10% less of it was used, and the strength of the concrete was almost 1.5 times less than in concrete containing ordinary portland cement of the same activity. At age 7 days the concrete strength in percent of the strength of concrete of age 28 days was noticeably less than that of concrete mixed using ordinary portland cement. Subsequently by age 90 and 180 days some increase in the rate of strengthening is observed compared to concrete strength at age 28 days. This indicates that it is not feasible to add plasticizing (workability) agents from the point of view of accelerating concrete hardening. As the water-cement ratio drops the intensity of hardening increases for a plasticized cement as well as for ordinary portland cement. In this case the absolute value of concrete strength increases as the W/C decreases to a greater degree than in ordinary portland cement.

V. V. Stolnikov [55] cites a comparison of the intensity of the strength increase of concrete containing ordinary and plasticized portland cements from which it is apparent that hardening is retarded in the initial periods in concrete with workability agents, and age 3 years the strength increase factor was practically identical.

TABLE 5.2. STRENGTH INCREASE OF CONCRETES MIXED USING VARIOUS CEMENTS WITH TIME

Cement	Concrete composition by volume and W/C	Compression strength at age							
		days					years		
		1	3	7	28	180	1	2	5
Grade 300 bauxite cement	1 : 2.48 : 4.05 W/C=0.68	$\frac{14.8}{51}$	$\frac{21}{72}$	$\frac{25.8}{89}$	$\frac{29}{100}$	$\frac{29}{100}$	$\frac{31.6}{109}$	—	$\frac{32.2}{111}$
Grade 400 portland cement ( $C_3S = 61.5\%$ )	W/C=0.71	—	$\frac{9}{29}$	$\frac{16.4}{53}$	$\frac{31}{100}$	$\frac{36.9}{119}$	$\frac{40.5}{130}$	$\frac{43.6}{142}$	—
Grade 400 portland cement ( $C_3S = 49\%$ )	W/C=0.72	—	$\frac{5.4}{27}$	$\frac{10.8}{55}$	$\frac{19.8}{100}$	$\frac{24.8}{125}$	$\frac{31.0}{156}$	$\frac{31.3}{158}$	$\frac{31.4}{153}$
Grade 300 portland cement ( $C_3S = 38\%$ )	W/C=0.78	—	$\frac{2.2}{18.3}$	$\frac{5.3}{41}$	$\frac{12}{100}$	$\frac{20.1}{107.5}$	—	$\frac{21.7}{181}$	—
Grade 250 portland cement ( $C_3S = 19\%$ )	W/C=0.78	$\frac{1.1}{10.3}$	$\frac{2}{18.7}$	$\frac{5.3}{49.5}$	$\frac{10.7}{100}$	$\frac{16.8}{157}$	$\frac{21.5}{201}$	$\frac{24.4}{228}$	—

Note. Numerator shows strength in MPa, denominator shows strength in % of  $R_{28}$ . Commas indicate decimal points.

The hardening rate of concrete containing slag portland cement is approximately the same as in concrete containing plastificized portland cement.

Approximately the same rate of strength increase of concrete in time is established when examining the many experimental data obtained by G. M. Rushchuk (All Union State Scientific Research and Planning Institute of the Cement Industry). Here it should be noted that pozzuolanic and pozzuolanicized portland cements demonstrated a considerable increase in concrete strength up to age 1 year. Thus, the average increase in strength of concrete containing grade 400 pozzuolanicized factor portland cement at age 1 year is characterized by a factor of 1.64, and that of concrete containing grade 250-300 pozzuolanic portland cement (with 30% tripoli added) increased to 2.08, i.e., the strength of the concrete during hardening under normal conditions doubled in a year.

Table 5.2 compiled from the results of experiments carried out by the author and N. I. Kukuyeva is given for the characteristics of the strength increase of concrete containing various cements under normal conditions.

Results of tests on strictly normally hardened concrete containing 5 cements are cited in the table. The samples were cured at the same time under air conditions and in water. The rate of strength increase up to

age 1-2 years for cements of rather characteristic types and activity is apparent from the table. Bauxite cement at age 1 day ensured strength equal to half the grade of the concrete.

Up to age 1 month portland cements ensured a concrete strength which was greater the higher their activity and the more  $C_3S$  contained in the cement clinker. Subsequently, i.e., after age 1 month, cements containing a smaller percentage of  $C_3S$  (accordingly with an increased content of  $C_2S$ ) yielded a higher percentage of strength increase.

#### Increase in Concrete Strength During 12.5 and 20 Years.

In 1948 in the laboratory of concretes and cements of the Central Scientific Research Institute of Industrial Structures the author and M. I. Kukuyeva prepared samples of concrete  $10 \times 10 \times 10$  cm, samples of mortar  $7 \times 7 \times 7$  cm, figure eights, as well as samples of cement paste of normal thickness  $3.16 \times 3.16 \times 3.16$  cm and figure eights.

The test samples were prepared from 7 cements of various mineralogical and material composition. The bauxite and slag bauxite (50% furnace slag and 50% cement) cements were obtained from the Pashiyskiy Factory. Three portland cements were obtained from the Voskresenskiy, Volskiy and Polski Cement Factories. The portland cements from Voskresenskiy and Polski Factories were grades 400, and that from the Volskiy Factory grade 250. Sorel slag portland cement from the Podolskiy Factory which had remained on site and whose activity had dropped to grade 150 was also used. The grade 300 pozzuolanic portland cement was delivered by elevator.

River sand with a size modulus of 2.35 and ordinary gravel, size approximately 25 mm, were used as aggregates for the concrete. The sand contained 1.5% pulverulent particles, the gravel 1.9%. The concrete samples were made to a composition of 1:2.48:4.05 with 3-4 cm slump using  $250 \text{ kg/m}^3$  cement. The materials were proportioned by mass and mixed in a concrete mixer with a capacity of 250 liters for 2-3 minutes. The concrete mixture was placed in metal forms with the aid of vibration on a laboratory platform with 30 seconds.

The prepared samples were kept 1 day in the forms at  $15-20^\circ\text{C}$ , except for the samples of pozzuolanic portland cement which were removed from the forms after 3 days. After striking the samples were sent for air, air-humidity and water storage. The cubes were compression tested at age: 1, 3, 7, 28, 180 days and 1, 3, 5, 10 and 12.5 years.

The samples were located in a closed chamber on racks for the air storage. The humidity varied from 60-80%. Air-humidity storage was effected in a standard storage chamber in which the air humidity was maintained at approximately 90-95%.

The samples were placed in deep iron pans for water storage. In the summer the temperature in the chambers was  $18-22^\circ\text{C}$  and during cold weather  $12-15^\circ\text{C}$ .



It should be noted that the temperature was maintained within 17-20° in the chambers for the first 28 days in all cases, to avoid the considerable effect of temperature variations on sample hardening at an early age.

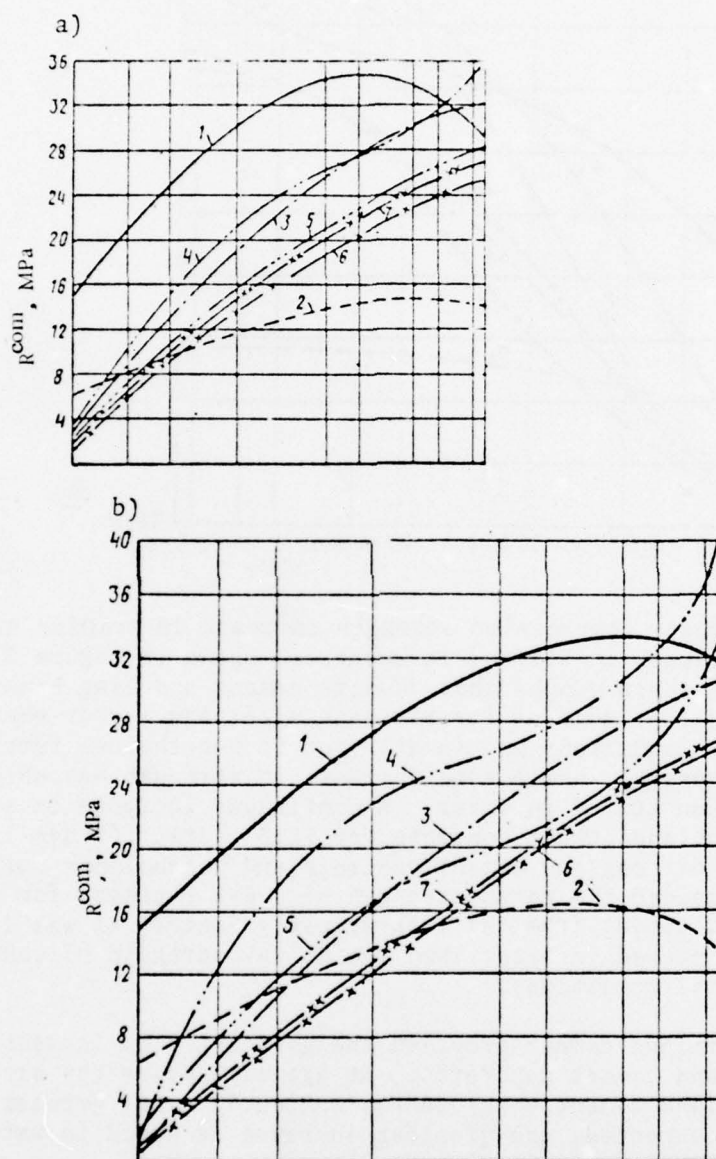
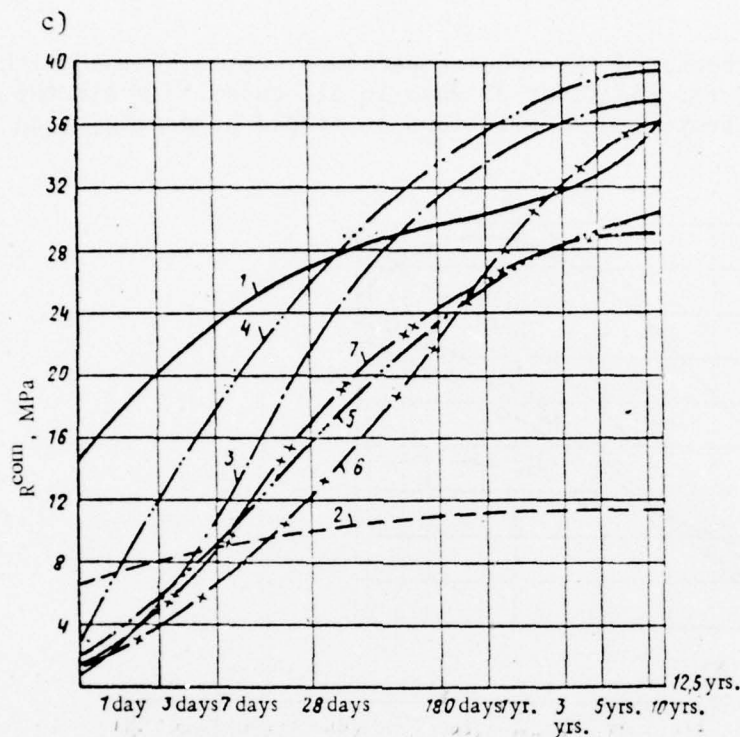


Figure 5.2. Strength Increase of Concretes Stored 12.5 Years Under Various Conditions. a, Normal; b, Air; c, Water. Concretes containing cements: 1, Bauxite; 2, Slag bauxite; 3, Portland cement from the Volskiy Factory; 4, The same, from the Polskiy Factory; 5, The same, from the Voskresenskiy Factory; 6, Sorel slag portland cement; 7, Pozzuolanic portland cement. [Figure continued on next page.]

[Continuation of Figure 5.2]



Graphs of concrete compression strength increase in samples stored under normal conditions, in air and in water are shown in Figure 5.2. It is apparent from these graphs that bauxite cement and slag bauxite cement concrete has lost some of its strength after age 1 year when stored under normal conditions and in air (but it nonetheless remained above the rated strength), while some increase in strength was observed up to 12.5 years when stored in water. A continuous increase in strength is observed for portland cement concrete for 12.5 years. At age 12.5 years the strength of portland cement concrete and pozzuolanic portland cement concrete exceeded the rated strength by 1.6-1.9 times; for concrete containing portland cement from the Voskresenskiy Factory it was 2.16 times greater when stored in water than the 28 day strength of concrete hardened under normal conditions.

Sorel slag portland cement provided the greatest time increase in strength for portland cement concretes. At age 12.5 years the strength of Sorel slag portland cement concrete was 2.22-2.72 times greater than the rated. As was expected, the greatest increase is noted in water storage.

Under more humid storage conditions the strength of the Volskiy portland cement concrete was higher in all hardening periods up to 12.5 years inclusive.

This conclusion cannot be applied to concretes mixed using other portland cements. For example, portland cement from the Voskresenskiy Factory with an increased aluminate content demonstrated the greatest increase in concrete strength under air storage conditions.

After age 1-5 years during dry air and normal storage the strength of bauxite cement concrete drops somewhat, and in water storage the strength increases continually.

At age 1 day bauxite cement concrete had 50%, and at age 7 days 86-89% of the 28 day strength of normally hardened samples assumed to be 100%. Subsequently an increase, although insignificant, in the rated strength of concrete containing this cement is observed. At age 3 days pozzuolanic portland cement concrete acquired 31%, and at age 7 days 54-58% of the rated strength. At this age the humidity conditions exerted no significant influence on the rate of strength increase of the concrete. Subsequently the best results were obtained with water storage.

Figure 5.3 shows the drop in strength of concrete mixed using Volskiy portland cement after storage in all media for 3 years. Some increase in strength occurs again after 10 years of storage. Upon more detailed examination of all experimental data on the testing of cement, mortar and concrete samples drops in strength in time are observed in all cases.

In 1940 samples of concrete containing grade 250 belite portland cement from the Chernorechenskiy Factory were prepared in the laboratory of concretes and cements of the Central Scientific Research Institute of Industrial Structures. Pozzuolanic and slag portland cements were made on the basis of this same cement. The concrete was used at a composition of 1:2.5:4.3 with cement consumption of 250 kg/m<sup>3</sup> at a W/C = 0.67-0.7. The concrete was prepared with a slump of 2-4 cm and consolidated on a platform vibrator in metal forms 7 × 7 × 7 cm. The concrete was cured under normal conditions, and subjected to steaming at 80°C and autoclave treatment at 170°C.

Samples were made using bauxite fused cement of composition 1:3.1:4.4 with cement consumption also 250 kg/m<sup>3</sup> at a W/C = 0.7 for normal hardening conditions in addition to those indicated. The workability of the mixture and the consolidation conditions are the same as in the portland cement concrete.

The samples were placed in a normal storage chamber, in a dry air chamber, in water and in earth after thermal treatment in the initial hardening period.

The compression strength of the concrete was tested immediately after thermal treatment, after 3, 7, 30 and 180 days. It was suggested that the concrete also be tested at age 2.5 and 10 years, but the author was not able to do this. Samples stored under normal conditions, in dry air and in water for more than 180 days, were lost. Only those samples which had been buried in the ground at a depth of 0.5-1 m were retained. After 18 years in the ground some of the samples were compression tested and the others were placed in a normal storage chamber. They remained there for 2 more years, and then were tested for strength at age 20 years. During the 18 year period the concrete samples under humid ground conditions were subjected to repeated freezing and thawing.



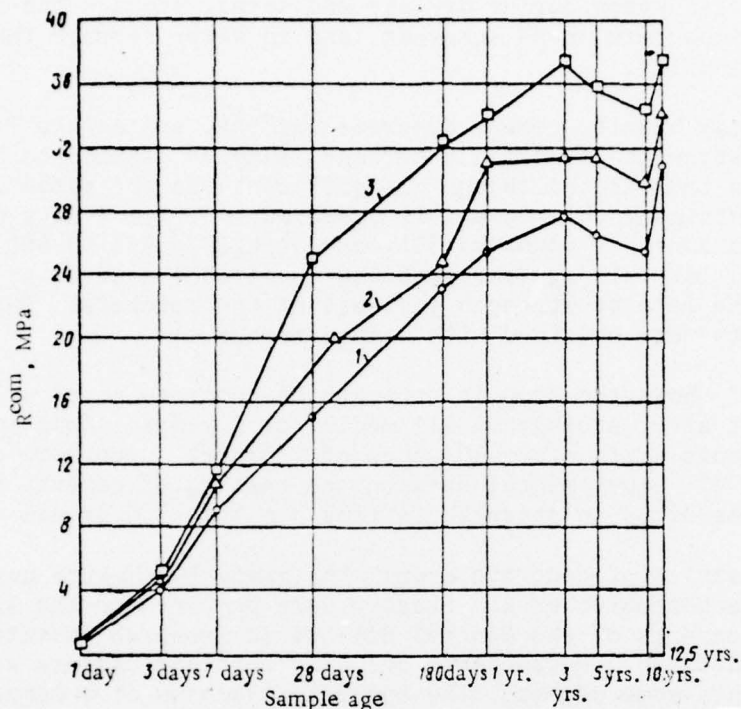


Figure 5.3. Strength Increase of Concrete Containing Portland Cement From the Volskiy Factory Under Different Storage Conditions. 1, Air; 2, Normal; 3, Water.

The results of the compression tests of the concrete cubes at age 7, 30, 180 days and 20 years are shown in Figures 5.4 and 5.5.

As can be seen from Figure 5.4, the strength of samples in the ground for 18 years continually increased. Upon subsequent normal storage for 2 years a small increase in strength was noted for concrete containing pozzuolanic and slag portland cement, and a drop in strength compared to the 18 year old concrete was observed in concrete containing bauxite and portland cements.

Concrete containing portland cement and bauxite cement at a normal temperature in a humid as well as in a dry air medium acquired the same strength in 1 month, and by age 6 months a relative lag in the increase in strength was discovered in concrete containing portland cement in a dry air state. The lag is apparently due to the fact that belite portland cement retains the ability to gain strength in time when it is stored in a humid medium. Strength lag in hardening under dry air conditions occurs in concretes containing pozzuolanic portland cement and to a somewhat lesser degree in those containing slag portland cement.

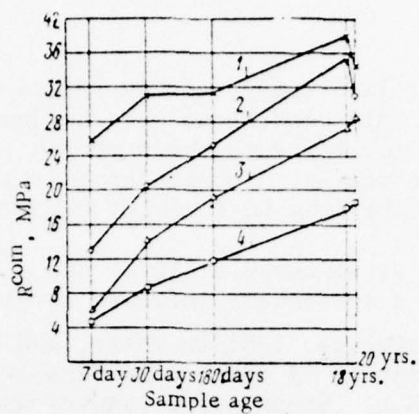


Figure 5.4. Strength Increase of Concrete Stored 18 Years in the Ground and 2 Years Under Normal Conditions. Concretes contain: 1, Bauxite cement; 2, Portland cement from the Chernorechenskiy Factory; 3, Pozzuolanic portland cement; 4, Slag portland cement.

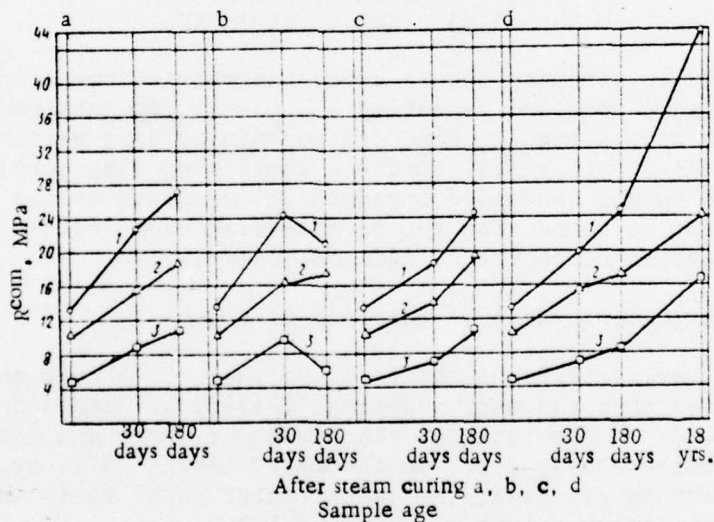


Figure 5.5. Strength Increase of Concrete Steam Cured at  $t = 80^{\circ}\text{C}$  and Then Stored Under Various Conditions. a, Normal; b, Dry air; c, Water; d, In the ground. The concretes contained: 1, Portland cement from the Chernorechenskiy Factory; 2, Pozzuolanic portland cement; 3, Slag portland cement.

Concrete containing portland cement without steam curing exhibited low sensitivity to various humid conditions when hardened up to 6 months. In the concrete underground for 18 years the strength increased 56% with time compared to that aged 6 months. Subsequent curing for 2 years under normal conditions even led to a drop in strength (Figure 5.5).

The same concrete, but steam cured at 80°C, had a strength of 76% of  $R_{30}$  after steam curing with a subsequent increase in strength to 153% at age 6 months during normal storage, 138% in water, and 141% in ground. Samples underground approximately 18 years considerably increased their strength which was 263% of  $R_{30}$ . Steam cured samples under dry air conditions increased strength to 137% at age 30 days with a drop to 119% at age 6 months.

Tests have shown that after thermal treatment under all humid conditions the compression strength continues to increase, except for the concrete steam cured and steamed with subsequent dry air storage; in this case a drop in strength by 18 and 58% respectively is observed by age 180 days.

Consequently, concrete containing belite portland cement after steam curing requires humid hardening conditions. At age 18 years steam cured as well as steamed concrete containing portland cement had a strength considerably greater than the 28 day (rated) strength.

If an increase in strength occurs after thermal treatment in concrete containing pozzuolanic portland cement in all cases upon subsequent storage, a drop in strength is observed in concrete containing slag portland cement by age 180 days. At age 18 years, concrete containing slag portland cement after steam curing increased strength 36% compared to the rated strength. It should be noted that the furnace slag used instead of the portland cement portion demonstrated reduced activity.

#### Effect of the Water-Cement Ratio on Concrete Strength.

Many studies, primarily those of I. G. Malyuga, D. Abrams and N. M. Belyayev, have shown that the most important quality of hardened concrete, its strength, depends on the ratio of the amount of water and cement, all other conditions being equal, i.e., on the water-cement (W/C) or, as has been more convenient in practice, the cement-water (C/W) ratio which determines the rectilinear nature of the dependency.

The dependency of concrete strength on the water-cement (cement-water) ratio is associated primarily with the structural formation process of the cement stone which occurs in conjunction with cement hydration. It is apparent that the strength of cement stone, and consequently concrete, should depend on the density of the cement stone. The more water in the cement stone, the less its strength, and consequently its density. However, the larger the water-cement ratio, the more free, unbound water remains and the greater the porosity of the concrete. An increase in the porosity of the concrete, inconsiderable even at first glance, inevitably causes a reduction in its strength.



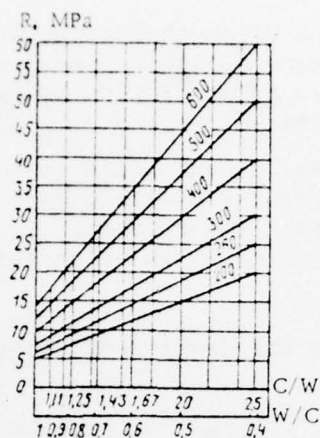


Figure 5.6. Limit of the Compression Strength of Concrete  $R_{con}$  on C/W and On the Cement Grade 200-600. Age - 28 days. Coarse aggregate - crushed granite.

The graphic dependency between the compression strength limit of concrete and the cement-water ratio is shown in Figure 5.6 (according to the data of I. P. Aleksandrin).

The formula of I. Bolomey who established the relationship between  $R_{con} - R_{cem} - C/W$  in the form of the linear function:

$$R_{con} = AR_{cem} (C/W - b),$$

where A and b are coefficients, is used in practice to calculate the concrete strength factor -- the value of C/W.

Testing of several cements used in concrete confirms the linear nature of the dependency and at the same time shows that coefficients A and b are different for different cements and even for cements of the same grade.

The average value of the coefficients when  $R_{cem}$  is determined experimentally in a wet mortar (according to GOST 310-60) was established on the basis of the experimental data of B. G. Scramtayev. The coefficients change as the procedure for testing the activity of the cements and the grades of the concretes changes. Apparently in conjunction with the rise in concrete grade in general and especially when manufacturing high strength concretes the average dependency can only be used to determine an approximate C/W value, the more so that the number of specialists who do not deny the linearity of the function believe that it consists of two straight-lines intersecting the x-axis at 2.5.

The author proceeds from the condition that while the C/W ratio in the concrete ensures the possibility of complete reactions between the cement and the water and the concrete mixture is well consolidated, and

the aggregates have sufficient strength for the appropriate grades of concrete, the function is a single line at least within the range from  $C/W = 3.3$  to  $C/W = 1.43$ . This point of view is engendered by the very nature of the relationship between  $C/W$  and  $R_{con}$  which is characterized by the degree of density of the cement stone in the concrete in which all spaces between aggregate fragments and grains are tightly filled and all their surfaces are covered with cement stone. In other words, what is meant is the strength of the material in which only the cement stone can be the sole loose component.

In conjunction with this the density of the concrete in fractions is expressed thusly:

$$D = 1 - \frac{W - \alpha C}{1000} = 1 - \frac{W - (1 - \alpha W/C)}{1000},$$

where  $D$  - density in fractions;

$W$  - water consumption in concrete in  $l/m^3$ ;

$C$  - cement consumption in concrete in  $kg/m^3$ ;

$\alpha$  - coefficient which shows the amount of mixing water which has reacted with cement in  $l/kg$ .

The linearity of the relationship  $R_{con}-C/W$  is apparent from this formula. The relationship for the case in which  $W = 200 l$  and  $\alpha = 0.2 l/kg$  is shown in Figure 5.7. It is also apparent that strength and density are interrelated.

The limit of line  $R_{con}-C/W$  at a  $C/W \geq 2.5$  may occur as the result of difficulties in the compact placement of concrete mixtures with a viscous cement paste. There already arises here the possibility of an insufficient water content for normal hydration of the cement. The validity of these considerations is confirmed by studies carried out at the Scientific-Research Institute of Concrete and Reinforced Concrete.

The curves of the strength increase of cement-containing concrete up to age 30 days are shown in Figure 5.8. The increase in concrete strength at different water-cement ratios was confirmed by a specially detailed study in the first 3 days of hardening. As is apparent from the data presented in Figure 5.8, when the  $W/C$  increases from 0.4 to 0.7, which corresponds to a drop in the  $C/W$  from 2.5 to 1.43, the concrete strength dropped almost three-fold. Tests show that as the  $W/C$  decreases to 0.4 with quality aggregates and methods of placing the concrete the grade of the latter may become approximately equal to the grade of the cement.

If the general principle of a reduction in concrete strength with an increase in  $W/C$  is retained, no direct proportionality between concrete strength and cement activity when using various cements is observed. This is explained by the difference in the mineralogical content, the

grinding fineness of the cement and the quality of the aggregates. After age 1 month, at which the grade of the concrete is usually determined, its strength increases as an identical function of W/C. In this case the larger the W/C value, the more the concrete strength increases. And conversely, as the W/C drops and the concrete grade rises the time increase in strength decreases. In quick-hardening concretes and concretes which harden under dry air conditions the increase in strength after 28 days is generally insignificant and decreases in it are observed.

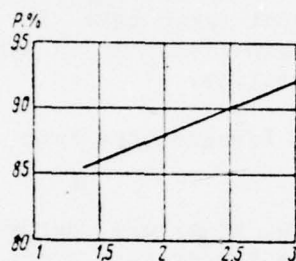


Figure 5.7. Theoretical Density of Concrete in % With Different Values of

W	C	$\alpha$	C/W	T, %
200	300	0.2	1.5	86
200	400	0.2	2	88
200	500	0.2	2.5	90
200	600	0.2	3	92

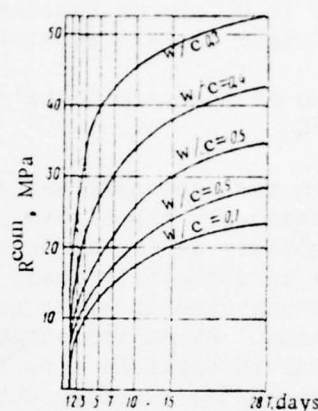


Figure 5.8. Strength of Concrete Containing Bryanskiy Grade 400 Portland Cement as a Function of W/C Under Normal Hardening Conditions.

The greatest increase in concrete strength occurs in a water and humid air medium. In concretes containing slag portland cements and pozzuolanic portland cements the strength increases more intensively after 28 days than in concretes containing portland cements. Concretes containing portland cements with a high  $C_3S$  content gain strength more rapidly during the early periods, and those containing cements with a high  $C_2S$  content at first harden slowly, however as time passes the intensity of strengthening comparatively increases. The results of the same experiments conducted by I. M. Frenkel and M. V. Teselkina at the Scientific Research Institute of Concrete and Reinforced Concrete are a good illustration of the gain in strength of concrete containing the same portland cement but at different W/C (Figure 5.8). In their experiments the concrete hardened under normal conditions. The water-cement ratio varied from 0.3 to 0.7. Upon careful examination it can be established that as the W/C decreased, the strength not only increased, but the rate at which it increased rose. Thus, for example, at age 1 day at a W/C = 0.7 concrete acquired 15% of its rated strength, at a W/C = 0.4 it was 24% of the rated strength, and at W/C = 0.3 it was already 35%. At age 2 days these strength values were at 32, 40 and 50% of that rated respectively.



The water-cement ratio was frequently reduced to accelerate hardening and at the same time increase the concrete grade. To avoid unjustified overconsumption of cement in doing this other technological methods are ordinarily used which result in an acceleration of concrete hardening. The use of stiffer concrete mixtures with a reduced water content is of great importance to accelerate the hardening and increase the strength of concrete. It should be noted that as the W/C drops the strength losses of concrete after early freezing are considerably reduced. Consequently, during winter concreting we must attempt to reduce the amount of water added as much as possible. A drop in the water-cement ratio makes it possible to obtain an increased concrete strength (especially at an early age) and make it less sensitive to the action of freezing.

#### Hardening of Concrete Containing Various Cements at Temperatures From 1 to 40°C.

When the necessary humidity is present concrete, as a rule, hardens more intensively the higher its temperature. As the temperature drops and especially as it approaches 0°C concrete hardening is severely retarded; this has an especially great effect at an early age. This is explained by the sharp drop in water activity in the chemical reaction of interaction with cement. At an ambient temperature of 0°C an above-zero temperature is maintained for some time in the concrete as the result of the continuing cement hydration reaction which is accompanied by the liberation of heat.

The latent heat of ice formation prevents the critical point passing through 0°C. The freezing of water in concrete associated with its passage from a liquid to a solid state does not occur immediately when the temperature reaches 0°C, but considerably below. As was shown in Chapter 1, at sub-zero temperatures some of the water generally remains in the liquid phase, therefore the hardening of the concrete continues, although very slowly. In this case active cements containing an increased percentage of highly basic clinker minerals ensures that the concrete gains strength more rapidly. Low activity neat cements and cements with finely ground additives at temperatures near 0°C more sharply retard the hardening of mortars and concretes.

This question is of great practical significance for operations under winter as well as fall and spring conditions. Operating methods should be selected with the consideration of the sharp retardation of mortar and concrete hardening as the temperature approaches 0°C. Additives, hardening accelerators, and salts which lower the freezing point of the liquid phase in the concrete play a significant role in these situations. More active and highly exothermic cements should be used under these conditions to simplify operating methods and to ensure the proper concrete quality.

As the temperature increases the hardening rate of concretes containing all cements increases, and therefore the requirements for cement activity and additive content change. When establishing the periods for removing the form-work and partial or complete loading of structures the rate of strength increase of concrete containing cements of various types and grades depending on temperature within 0 to 40°C may be taken from Table 5.3.

TABLE 5.3. RELATIVE COMPRESSION STRENGTH OF CONCRETE  
AT DIFFERENT HARDENING TEMPERATURES, % OF 28 DAY STRENGTH  
(HARDENING AT T = 20°C AND W = 90-100%)

Concrete	Harden- ing time, days	Average concrete temperature, °C						
		-3	0	5	10	20	30	40
Grade 200 containing grade 300 portland cement	1	—	4	6	10	18	27	36
	2	—	8	12	18	30	43	55
	3	5	12	20	25	40	52	65
	5	8	20	30	40	55	65	78
	7	10	30	40	50	65	74	85
	14	12	40	55	65	80	90	100
	28	15	55	68	80	100	—	—
Grades 200-300 containing grade 400 portland cement	1	3	5	9	12	23	35	45
	2	6	12	19	25	40	55	65
	3	8	18	27	37	50	65	77
	5	12	28	38	50	65	80	90
	7	15	35	48	58	75	90	100
	14	20	50	62	72	90	100	—
	28	25	65	77	85	100	—	—
Grade 400 containing grade 500 portland cement	1	—	8	12	18	28	40	55
	2	—	16	22	32	50	63	75
	3	10	22	32	45	60	74	85
	5	16	32	45	58	74	85	96
	7	19	40	55	66	82	92	100
	14	25	57	70	80	92	100	—
	28	30	70	80	90	100	—	—
Grade 500 containing grade 600 portland cement	1	—	9	13	21	32	45	59
	2	—	17	25	36	52	65	75
	3	—	23	35	46	62	75	85
	5	—	34	47	58	75	83	90
	7	20	42	57	68	85	90	100
	14	30	58	73	82	95	100	—
	28	35	75	83	92	100	—	—
Grade 200 containing grade 300 portland cement	1	—	—	3	6	12	20	35
	2	—	4	7	12	20	35	50
	3	2	7	12	18	30	46	63
	5	4	13	20	30	45	60	80
	7	6	18	25	40	55	70	92
	14	8	25	40	55	75	90	—
	28	10	35	55	70	100	—	—
Grades 200-300 containing grade 400 slag portland cement	1	—	3	6	10	16	30	40
	2	3	8	12	18	30	40	60
	3	5	13	18	25	40	55	70
	5	8	20	27	35	55	65	85
	7	10	25	34	43	65	70	100
	14	12	35	50	60	80	96	—
	28	15	45	65	80	100	—	—

The data cited in this table are averages derived from a large number of tests conducted in the laboratory for acceleration of concrete hardening of the Scientific Research Institute of Concrete and Reinforced Concrete in 1971-1974 and they refine the values of gain of relative strength up to age 28 days compared to data published in the preceding edition which was based on experiments in 1939-1941 with some refinement of the work in 1949-1950 when cement grades were different from those today. The kinetics of strength increase were established for concretes prepared from mixtures with a workability of 6-8 cm of slump.

Results were used in compiling Table 5.3 which were obtained from studies of hardening of concrete prepared from mixtures with a slump of 1-3 cm. Graphs are given for convenience in using these data to calculate the strength increase of concretes up to age 28 days (Figure 5.9). The consumptions and grades of cements are accepted to be those most frequently used on cast in situ construction sites. When using portland cements containing more than 6% tricalcium aluminate, the rate of strength increase compared to the data cited in Table 5.3 and on the graphs increased approximately 10%. The difference in the rate of strengthening of concrete containing 2 cements of the same grade, but with a different content of  $C_3A$ , is shown in Table 5.4.

Recently lightweight concretes have begun to be used in erecting cast in situ structures; therefore special experiments were conducted to study the rate of strengthening of light aggregate concrete and agloporite concrete (Table 5.5) at from  $-3$  to  $40^{\circ}C$ .

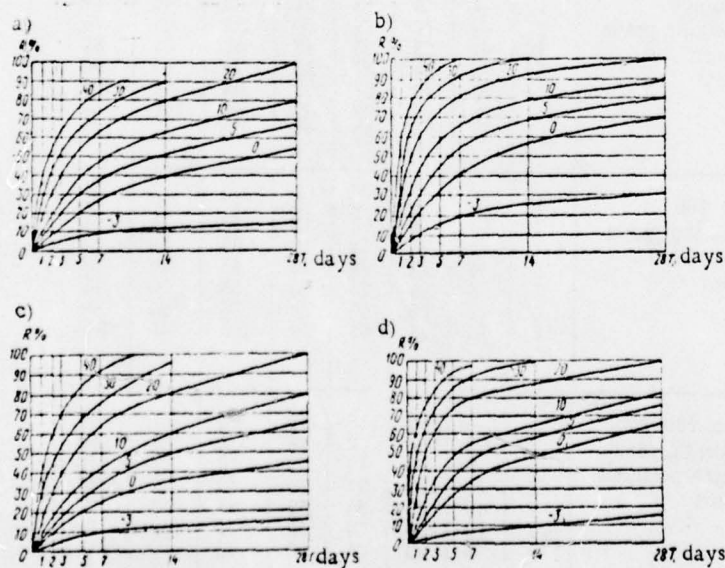


Figure 5.9. Increase in Concrete Strength From  $-3$  to  $+40^{\circ}C$ .  
a, Grade 200 concrete containing grade 300 portland cement;  
b, Grade 400 concrete containing grade 500 portland cement;  
c, Grade 200-300 concrete containing grade 400 slag portland cement;  
d, Grade 200 lightweight concrete containing grade 400 portland cement.



TABLE 5.4. INCREASE IN STRENGTH OF GRADES 200-300 CONCRETE CONTAINING GRADE 400 PORTLAND CEMENT FROM THE BELGOROD AND VOSKRESENSKIY FACTORIES

Concrete age, days	Average concrete temperature in the structure, °C													
	-3		0		5		10		20		30		40	
	B	V	B	V	B	V	B	V	B	V	B	V	B	V
1/2	—	—	2	2	4	4	6	6	10	14	15	25	25	30
1	2	4	5	6	9	12	12	14	22	28	41	48	53	55
2	5	6	10	14	18	24	26	30	40	48	53	63	70	70
3	8	10	18	22	25	32	35	40	50	60	69	75	85	90
5	14	17	28	35	38	46	50	55	65	70	81	85	98	98
7	18	20	37	43	48	53	56	60	75	80	91	95	100	102
14	20	25	51	59	67	72	72	80	87	92	104	105	—	—
28	25	30	70	75	84	85	93	93	100	100	—	—	—	—

Note. B - Portland cement from the Belgorod Factory ( $C_3A < 6\%$ );  
V - The same from the Voskresenskiy Factory ( $C_3A > 6\%$ ).

Average data on the increase in strength of concretes containing porous lightweight aggregates are cited in Figure 5.9, d. As the temperature drops the hardening of concrete containing slag portland cement, just as that containing pozzuolanic portland cement, is retarded more significantly than concrete containing portland cement. It should be kept in mind that the rates of strength increase may differ substantially from those shown in the tables and on the graphs depending on the mineralogical content of the cement clinker, introduced ground additives, workability of the mixtures being placed, and the water-cement ratio. For example, as the water-cement ratio changes, especially in the early periods, the rate of strength increase in the concrete differs quite substantially from average data (Table 5.6).

TABLE 5.5. STRENGTH INCREASE OF GRADE 200 LIGHTWEIGHT CONCRETE CONTAINING GRADE 400 PORTLAND CEMENT, %

Concrete age, days	Average concrete temperature in the structure, °C													
	-3		0		5		10		20		30		40	
	K	A	K	A	K	A	K	A	K	A	K	A	K	A
1	1	2	3	3	5	6	10	10	25	24	50	48	61	61
2	3	4	9	11	14	13	24	26	50	50	63	65	75	76
3	4	5	18	20	23	24	37	40	63	62	73	75	85	86
7	6	7	35	37	48	45	58	53	80	80	91	91	97	97
28	15	16	65	67	79	73	83	82	100	100	—	—	—	—

Note. K - Lightweight aggregate [haydite] concrete; A - Agloporite concrete.

In deciding the question of removing the form-work or loading concrete in reinforced concrete structures, it is very important to have data not only about the temperature conditions of concrete hardening, but also the results of strength tests of control samples stored if possible under conditions near those of production. Such laboratory tests make it possible to discover more exactly the strength of concrete considering local conditions on actual compositions and materials. The time change of concrete strength takes place in accordance with a general principle: at first an intensive increase in strength up to a certain optimum, and then a gradual decrease in the rate of its growth. Rapid strengthening occurs at the stage of development of the "avalanche" process of cement hydration, later strengthening during a certain period depending on various factors, after which the intensity of strength increase of concrete decreases.

TABLE 5.6. KINETICS OF THE INCREASE IN CONCRETE STRENGTH DEPENDING ON THE CEMENT-WATER RATIO

C/W	Concrete strength, % of cement activity in age, days				W/C
	1	2	3	28	
3.33	30	47	57	110	0.3
2.86	28	45	55	100	0.35
2.5	25	38	48	80	0.4
2.22	20	32	40	70	0.45
2	16	27	34	63	0.5
1.81	14	22	28	56	0.55
1.67	12	19	25	50	0.6

Commas indicate decimal points.

#### Hardening of Concrete Containing Various Cements at From 40 to 100°C.

Initial curing at reduced above zero temperatures, and then under normal conditions or at increased temperatures, forms the optimum conditions for hardening concrete from the point of view of a further increase in its strength. However, under winter conditions and in a number of cases of rapid construction, not to mention factory and casting yard manufacture of prefabricated reinforced concrete building elements, there is an extreme need to accelerate the hardening times of concrete after placing it. For these reasons the use of some method of thermal treatment of concrete at an early age is usually needed. As our studies have shown, the thermal treatment conditions should be chosen depending on the types of cements and their mineralogical composition, aggregates, the water-cement ratio, and the consistency of the concrete mixture.

The efficiency of the various methods of thermal treatment is not identical. For example, steam curing concrete with a suitable combination of high temperature and atmospheric humidity leads to better results than electrical heating and dry air heating. As the temperature increases and the thermal treatment periods lengthen as well as in using cements with ground additives instead of pure neat cements, the effect of steam curing

concrete is heightened. In many cases heating of concrete containing portland cement (especially high aluminate) at 50°C and above causes a drop in strength compared to the strength of concrete which was normally hardened; this drop reaches 25% under unfavorable conditions. Therefore in due time it was suggested in these cases that preliminary curing of the concrete at reduced temperatures be used before beginning the heating. Low activity (with an increased  $C_2S$  content) and mixed portland cements under a favorable concrete moisture condition do not lower its strength during heating, but conversely, increase it compared with the rated strength. The relative strength of concrete cured up to 28 days, after steam curing or electrical heating, is usually (percent of the strength of concrete normally hardened for 28 days):

Containing portland cement	80-110
Containing pozzuolanic portland cement	90-115
Containing slag portland cement	100-130

In this case the strength produced is calculated immediately after thermal treatment of the concrete and subsequently when hardening it up to age 28 days under normal conditions. Consequently, when selecting a concrete composition it is necessary to consider the effect of hygrothermal treatment on the actually obtained concrete strength.

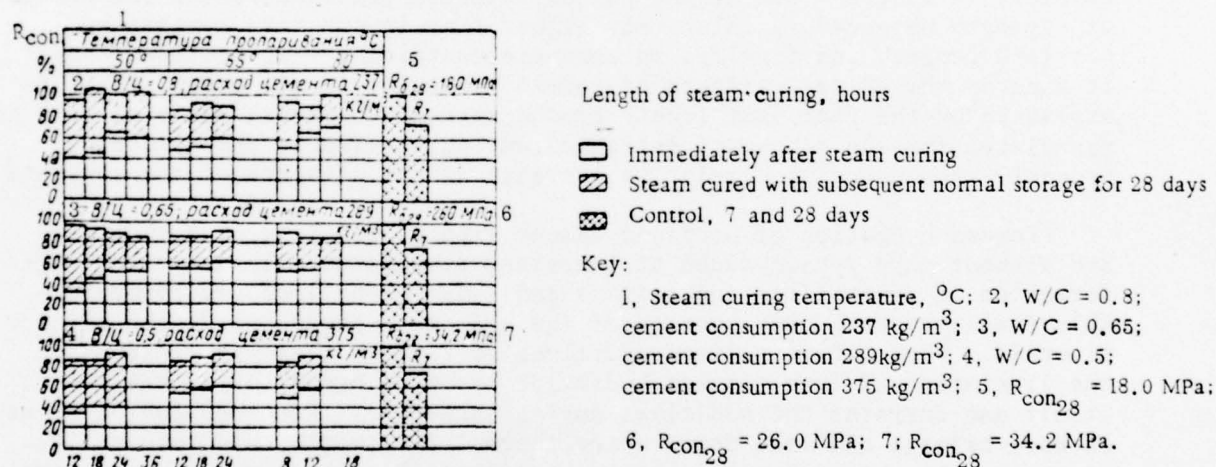


Figure 5.10. Strength of Concrete Containing Grade 400 Portland Cement Depending on the Length of Steam Curing at Different Temperatures, % of  $R_{28}$ .

In most cases the so-called delivery strength determined 12 hours after the completion of thermal treatment is of special importance in the thermal treatment of concrete at factories and casting yards for reinforced concrete structural elements.



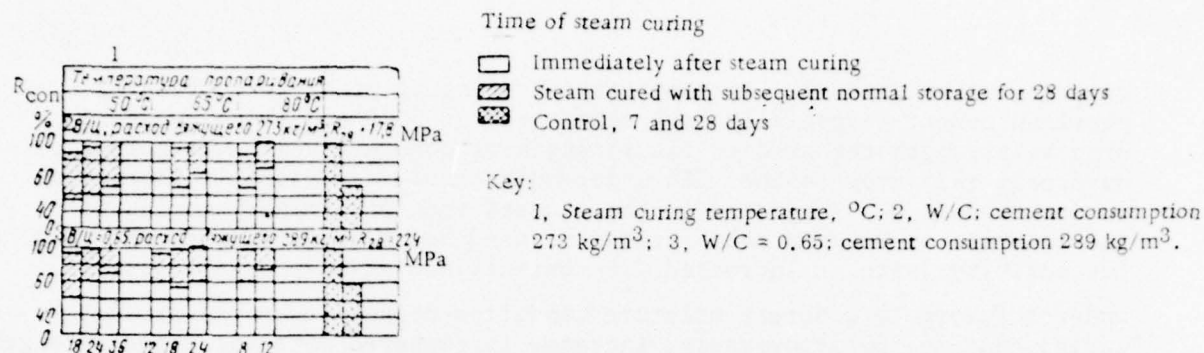


Figure 5.11. Strength of Concrete Containing Grade 400 Pozzuoalanic Portland Cement Depending on the Length of Steam Curing at Different Temperatures, % of  $R_{28}$ .

Data on the strength of concrete containing three types of cement in percentages of  $R_{28}$  depending on temperature and length of steam curing are shown in Figures 5.10, 5.11, 5.12. It is clear from these diagrams that in concrete containing portland cement incomplete strengthening is apparent by age 28 days after steam curing compared to normally hardening samples; in concrete containing pozzuoalanicized portland cement the percent of strength obtained is relatively higher than in concrete containing portland cement, and finally, in concrete containing slag portland cement it exceeds the 28 day strength of normal hardening in all cases. This is explained by the fact that finely ground active additives, and even more so granulated furnace slags are entrained during heating in the hardening process, thus ensuring a relative increase in the strength of the concrete.

Forced hydration of portland cement without finely ground additives and without more gypsum added at increased temperatures leads to the rapid formation of crystalline concretions and a dense shell of new formations. This shell prevents continuation of the hydration processes of the clinker minerals. When active silicon additives or furnace slags are introduced, the liberation of free calcium hydroxide promotes hydration of the cement itself and entrains the additives during hardening. Portland cement stone is more brittle and less dense after thermal treatment; this reduces its strength. We obtain better results by adding 2% calcium chloride or more gypsum. In these cases high strength was obtained upon heating, and no subsequent drop in concrete strength was observed. When using quick hardening cements, stiff mixtures and richer concrete compositions the intensity of the growth in concrete strength increases. With regard to considerations of optimum conditions for hardening concrete, a temperature below 60°C may be used only when using high aluminate and quick hardening portland cements.

Additional acceleration of its hardening is not achieved when thermally treating concrete containing bauxite cement. Therefore this cement, as a rule, should not be thermally treated.

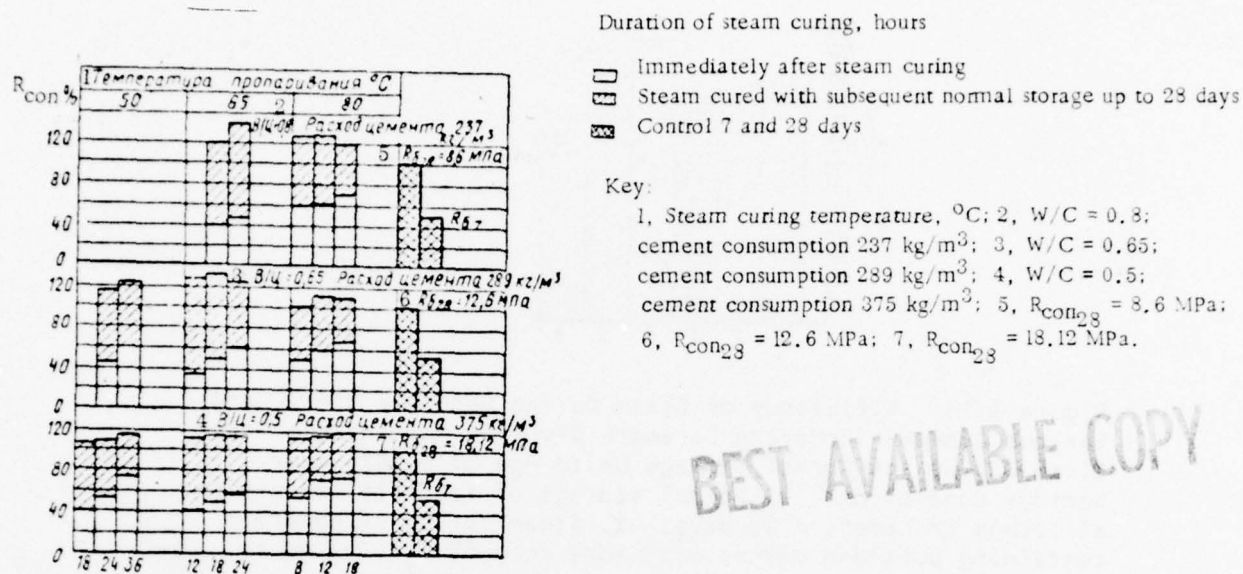


Figure 5.12. Strength of Concrete Containing Grade 250 Slag Portland Cement As a Function of the Duration of Steam Curing at Different Temperatures in % of  $R_{28}$ .

The basic characteristic (grade) of concrete is accepted to be its compression strength limit. The rupture, bending, shock, abrasion and so forth strength limits of concrete are determined in an approximate manner from their proportional dependency on the compression strength limit. Some data on the characteristic of concrete strength not only during bending, but during other types of testing, are cited below.

The diagram of the comparative strength of concrete at age 28 days after it has undergone hygrothermal treatment has been constructed to generalize the nature of the behavior of different cements during thermal treatment (Figure 5.13). The greatest effect is achieved when using slag portland cement and pozzuolanic portland cement and the least when using bauxite cement.

The strength of concretes containing all types of cements which is obtained during normal 28-day storage is accepted as 100% on the diagram. The strength (in percentages) of concretes subjected to thermal treatment and then hardened up to 28 days under normal conditions is compared to  $R_{28}$  of normal hardening in all cases. If we consider that thermal treatment of concrete exerts a dissimilar effect on cements of the same type and grade, it is recommended that before beginning operations test thermal treatment of concrete samples containing the cement available at the site at the required temperatures be conducted.

The composition of concrete and the consumption of cement are being refined as the result of these experiments. In doing this it may be that when heating it is necessary to reduce the consumption of slag portland cement, and increase the consumption of certain portland cements compared to the cement consumption specified for normal hardening conditions.

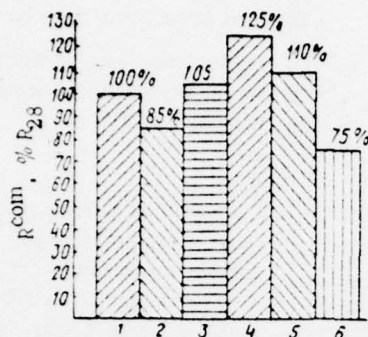


Figure 5.13. Efficiency of Steam Curing Concrete Containing Various Cements (Concrete Strength Given in Percentages After Steam Curing and Normal Storage Up to Age 28 days) Under Various Conditions. 1, Normal storage of concrete containing all types of cement - 28 days; 2, Steam curing of concrete containing portland cement with more than 8%  $C_3A$  1-2 hours after placement; 3, 8-12 hours of curing of concrete before steam curing or addition of gypsum; 4, Steam curing of concrete containing slag portland cement; 5, The same containing pozzuolanic portland cement; 6, The same containing bauxite cement.

The efficiency of heating concrete with various cement consumptions, and consequently water-cement ratio, is not the same. As the water-cement ratio decreases intensity of concrete hardening grows. Thus, for example, when  $300 \text{ kg/m}^3$  grades 400-500 portland cement are consumed, after 12 hours of steam curing at  $t = 80^\circ\text{C}$  the concrete strength is 50% of  $R_{28}$ , and when  $500 \text{ kg/m}^3$  are consumed it increases to 65%.

As the cement consumption drops to  $200\text{-}250 \text{ kg/m}^3$  the intensity with which the concrete gains strength drops (Figure 5.14). This is due to the fact that a cement paste, just as any mineral glue, hardens more quickly as the stiffness increases. The dependency of concrete strength when steam cured on cement consumption shown in the figure was obtained in working with concrete mixtures with a slump of 2-3 cm.

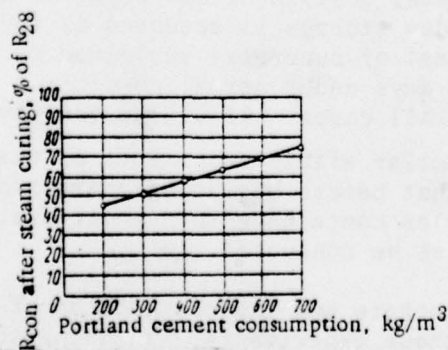


Figure 5.14. Intensity of the Increase in Concrete Strength During Steam Curing as a Function of Cement Consumption.



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TABLE 5.7. DEPENDENCY OF THE COMPRESSION STRENGTH LIMIT OF CONCRETE ON THE LENGTH OF STEAM CURING AT 80°C

Cement	Total cement consum. in kg per 1 m <sup>3</sup> conc.	Cement composition		W/C	Stumping of a standard cone, cm	Concrete strength, 28 days normal, MPa	Length of isothermal heating, hours	Strength of sample 10 x 10 x 10 cm, MPa, after			Concrete strength, % of grade of conc. contain. same cement, at age			Concrete strength, % of grade of conc. contain. cement w/o additive, at age		
		Component	Content, %					3 hrs.	25 days	90 days	3 hrs.	25 days	90 days	3 hrs.	25 days	90 days
Portland cement from the Voskresenskiy Factory	300	Portland cement	100	0.48	1	33.3	7	22.1	30.2	37.4	66	91	113	66	91	113
		Portland cement, tripoli	75	0.66	1.5	23.6	13	23.2	32.3	37.8	74	97	104	70	97	104
		Portland cement, granulated slag	70	0.46	1	31.6	19	21.7	26.8	34.5	101	111	131	67	80	100
Portland cement from the Belgorod Factory	300	Portland cement	100	0.5	3.5	29.2	7	16.3	35.1	45.8	73	97	111	76	101	115
		Portland cement, tripoli	75	0.67	2.5	20.6	13	20.6	30.7	35.3	86	109	117	89	114	121
		Portland cement, granulated slag	70	0.5	4	32.2	19	21.7	23.8	28.4	116	102	137	82	72	97
Portland cement from the Belgorod Factory	500	Portland cement	100	0.34	5	54	7	39.7	60.1	61.3	71	111	117	73	111	117
		Portland cement, tripoli	75	0.52	0.5	32.9	13	43.7	56.9	62.4	80	105	116	80	105	116
		Portland cement, granulated slag	70	0.37	7	48.4	19	30.7	47.7	55.4	91	100	105	57	64	65
Slag portland cement	300	Slag portland cement	100	0.51	3	19.3	7	13	23.8	27.1	67	121	137	67	121	137
		Same	100	0.37	3.5	21.8	13	16.6	27.1	25.4	91	100	120	86	100	120
		Same	100	0.37	3.5	21.8	19	20.7	39.7	42.6	83	100	121	83	100	121

Remarks: 1. Average concrete curing time before steam curing was 4-5 hours.

2. Temperature increased to 80°C for 3 hours.

3. Samples cooled outside the steam curing chamber 3 hours at an air temperature of 20-25°C.

Commas indicate decimal points.

At the present time the quality of concrete has considerably improved at the same time that factory output has increased. The average activity of cement exceeds 40 MPa. According to factory data on the mineralogical content of portland cement clinkers, the content of tricalcium silicate in them has increased to 50-65% in most cases. The grinding fineness of cement is increasing and calcining of cement clinker is improving. The aluminate content of cements has dropped due to the change to liquid fuel (instead of powdered coal). The introduction of active ground additives is increasing the efficiency of thermal treatment of concrete of reinforced concrete structures; however, this reduces its rated strength.

Steam curing times can be considerably reduced by using stiff concrete mixtures with a reduced water-cement ratio. The results of tests conducted by the author and G. A. Arobelidze on concrete containing various cements after steam curing at 80°C for 7, 13 and 19 hours are cited in Table 5.7.

As tests have shown, increasing the temperature to 95°C does not in actuality lead to an acceleration in the hardening of concrete containing factory portland cements. The introduction of additives to portland cement in an amount of 25% finely ground tripoli or granulated slag ensures the efficiency of increasing the temperature of steam curing to 95°C.

Steam curing of concrete containing a high grade cement with a low W/C at 80°C for 7 hours (plus 3 hours to raise the temperature and 3 hours for cooling) as a rule produces a concrete strength of approximately 50-75% of  $R_{28}$ . As the length of steam curing of the concrete increases from 7 to 13 hours the strength subsequently increases to 70-80% of  $R_{28}$ . Thus, the efficiency of increasing the steam curing times of this concrete drops. A longer thermal treatment time for this concrete at 80°C was completely unfeasible. It should be noted that in these cases the consumption of portland cement was 300 and 500 kg/m<sup>3</sup>, and the low workability concrete was mixed using granite gravel and good quality Moscow River sand.

When finely ground granulated slag is added the efficiency of steam curing lasts approximately one day, and when ground tripoli is added 12 hours. The effect of brief steam curing increases as the water-cement ratio decreases and the stiffness of the concrete mixture being placed increases. Consequently, steam curing times can be significantly reduced when working with high strength concretes.

#### The Effect of Adding Furnace Slags on the Strength of Concrete Containing Slag Portland Cement.

The use of slag portland cement when conducting concrete and reinforced concrete operations in winter is undesirable in most cases. An exception is the placement of concrete in massive structures and the use of thermal treatment. In other cases only quick-hardening slag portland cements of a higher grade are needed at sub-zero temperatures. Unfortunately, a large amount of low grade slag portland cements are delivered to winter sites at the present time. This raises costs and complicates production methods,

and leads to prolonged curing of cast in situ structures before dismantling the form-work. It is desirable that slag portland cements arriving at winter sites contain a reduced amount of slag added to the cement.

Our experience in using them began in the 1930's [47]. It is produced in rather large quantities in the FRG, the GDR, Belgium, France, Poland, Czechoslovakia and other countries in consideration of the economy of this cement, since slag products from the metallurgical industry are used in making it. Slag portland cement is economical to use in erecting blocks (dams, foundations), when placing concrete in aggressive media, especially in sulfate waters. For example, slag portland cement was used to restore the damaged Dnepr Hydroelectric Station dam, in erecting the Kakhovskaya Hydroelectric Station dam and others.

For the construction of the Kakhovskaya Hydroelectric Station the author tested concretes containing slag portland cement for strength and resistance to freezing. Recommendations were made to increase the strength and frost resistance of concretes prepared from highly workable mixtures.

In one of the first documents standardizing concrete steam curing the author noted in 1938 that the greatest effect of steam curing compared to normal hardening takes place when using slag portland cement.

The intensity of hardening of cements with added furnace slags during steam curing as well as under normal conditions depends on the material and chemical-mineralogical composition of the components (cement and slag), their dispersion and granulometric composition, microstructure, etc.

There are very many diverse factors which effect the nature of hardening of slag portland cements, the components of which differ widely with regard to their hydraulic activity, grindability, and other characteristics. For example, the material composition of these cements may vary within considerable limits (according to the standard the allowable content of slag in slag portland cements is from 30 to 60%, and in some cases a content of 70% slag is permitted).

The hardening processes of slag portland cement, especially with a high slag content, compared to portland cements on the whole, are more complex, since their composition is more complex; the clinker and sulfate components in slag portland cements, in addition to their usual functions, promote the development of the latent hydraulic activity of granulated furnace slags as well.

One of the most important factors which affect the properties and intensity of hardening of these cements is the dispersion and granulometric composition. At the present time the cement industry of the USSR manufactures primarily portland cements of comparatively low dispersion containing approximately 50% slag which are characterized by grades 200-400. Concretes containing these cements are distinguished by the slow gain of strength, especially under conditions of low above-zero and sub-zero temperatures.



Their use for producing precast reinforced concrete requires some lengthening of the isothermic period or 10-12% overconsumption of cement compared to portland cements of equal grade. In spite of this, the use of these concretes in a large number of cases is economically justified by their lower cost (for factory manufacture of reinforced concrete, in underwater hydrotechnical facilities, in facilities subject to the action of an aggressive, in particular sulfate, medium).

However, for intense hardening of slag portland cements it is necessary that their particle size be characterized by a specific surface of at least 3500-4000 cm<sup>2</sup>/g with a limited slag content in the cement (30-50%). These cements can be efficiently used to make concretes which harden under normal temperature conditions as well as during thermal treatment. In the laboratory for methods of accelerating concrete hardening of the Scientific Research Institute of Concrete and Reinforced Concrete, S. A. Vysotskiy and I. V. Smirnova conducted experiments on determining an efficient amount of slags in cements for thermal treatment of concretes. Cements [binders] used in the experiments were made by grinding together Voskresenskiy clinker and Tul'skiy slag, as well as Magnitogorskiy clinker and slag, granite gravel with a maximum particle size of 20 mm and quartz river sand with  $M_{ps} = 1.82$ . The experiments were conducted on concretes of two compositions -- 1:2.02:3.43 (W/C = 0.4) and 1:3.51:5.33 (W/C = 0.6) prepared from concrete mixtures of approximately the same stiffness (35-40 s). In doing this the concrete mixtures containing cement with an 80% slag content were characterized by somewhat greater stiffness (approximately 10 s) compared to neat cement. According to the data of the State All Union Scientific Research Institute of the Cement Industry, the physical-mechanical properties of cements used are cited in Table 5.8 from which it follows that the "dilution" of clinker with slag reduces the compression strength of the mortars; however in this case the tensile strength during bending remains on approximately the same level. Used as an additive, slag was highly active.

The data cited in Figure 5.15, a, b, indicate that under normal hardening conditions an increase in the slag content in cement up to 40% does not significantly affect the change in concrete strength; however in concretes with a W/C = 0.6 a tendency is observed toward a drop in strength. A further increase in slag content from 40 to 80% is accompanied by a sharp drop in concrete strength, 32-36%. The greater particle size of cement containing 40 and 80% slag, according to the indicator of residue on a sieve with 10,000 holes/cm<sup>2</sup>, with the same specific surface of the cement somewhat affected the results we obtained (see Table 5.8). Moreover, some researchers note a lesser content of crystalline calcium hydroxide; this is due to the bonding of Ca<sup>+2</sup> ions from the liquid phase of the hardening system by slag grains with the formation of gel-like masses of calcium hydrosilicates and also by the formation of a more dense hydrosilicate gel structure. This in turn is favorably reflected in the mechanical strength of concretes containing slag portland cement, especially in tensile strength. Here in mortar samples intended for determining cement activity, as the slag content in the cements increases the ratio of the bending strength to the compression strength apparently increases more than in concretes.

TABLE 5.8. PHYSICAL-MECHANICAL PROPERTIES OF CEMENTS CONTAINING CLINKER FROM THE VOSKRESENSKIY CEMENT FACTORY AND TULSKIY SLAG. ADDITION OF 5% GYPSUM OVER 100%.

Cement composit. by mass, %		Cement grinding of fineness			Normal thickness of cement paste, %	Setting times, hours-minutes		Cone spread mm	Strength MPa, during			
Clinker	Slag	Specific surface, cm <sup>2</sup> /g	Remainder on sieves, %			Start	Finish		Bending, at age, days		Compression, at age, days	
			0,045	0,033					7	28	7	28
100	0	3700	8,6	20	25,5	2	3—45	116	5,6	7	37,2	48,1
80	20	3760	6,7	17	25,75	2—40	3—55	116	6	6,5	35,2	46,9
60	40	3720	7	14	25,75	2—30	4—10	118	5,8	7	32,7	40,5
40	60	3540	6,4	17	26,75	3—50	5—35	119	4,8	7,4	27,2	—
20	80	3520	5,8	12	27,5	3—55	5—45	122	5,2	7,3	23,5	32,2
0	100	3583	2,7	12	28,25	4—25	9—40	122	4,5	5,5	11,8	14,7

Commas indicate decimal points.

Steam curing results in a considerable gain in strength by concretes containing cements with a high slag content. On the basis of these results we may conclude the strength of concretes containing cements with varying slag content 10-12 hours after steam curing is on approximately the same level (at a W/C = 0.4 as well as at a W/C = 0.6). Subsequent 27 day hardening of the concrete after steam curing under normal conditions proceeds variously depending on the material content of the cements and the water-cement ratio.

Concrete containing neat cement is 1.16 times stronger at W/C = 0.4 and 1.19 times at W/C = 0.6, that containing cement with 40% slag 1.22 and 1.31 times, respectively and that containing 80% slag 1.04 and 1.27 times. Apparently in cements with a high slag content the clinker component of the cement is exhausted to a considerable degree after steam curing, and the grains of clinker and slag which remain unhydrated are not able to provide a subsequent gain in strength under room temperature hardening conditions.

Consequently at age 28 days after steam curing the strength characteristics of concretes containing cements with a moderate slag content (40%), as a rule, exceed the corresponding indicators of concretes containing cements with a 60-80% slag content by 10-15%. It may be assumed that as hardening proceeds this difference will increase and the advantages of cements with a moderate slag content will become more pronounced.

In analyzing the data cited in Figure 5.15 it must be noted that in a number of cases the strength of steam cured concretes did not reach the rated strength by 28 days of subsequent hardening under normal conditions. For concrete containing neat cement this deficit was 8% at a W/C = 0.4 and 15% at a W/C = 0.6, for concrete containing cement with a 40% slag content 7-6%, while concrete containing 80% active, more finely ground slag considerably exceeded the rated strength (by approximately 20%) 10-12 hours after steam curing using a 3 + 6 + 3 hour system at 95°C. A similar phenomenon is explained by the destruction of the freshly molded concrete by temperature expansion of its components. However, in most cases the strength of steam cured concrete at age 28 days usually exceeded the rated strength (by 10-20% or more) when steam curing concretes containing slag portland cements using a similar system. This is apparently due to the use of factory slag portland cements of comparatively low activity (compared to that used in these experiments).

The mineralogical composition of the Voskresenskiy clinker which is generally distinguished by its increased  $C_3A$  content must also be taken into consideration. Under steam curing conditions this leads to the formation of a large crystalline skeleton of cubic  $C_3A \cdot 6H_2O$  with increased uniform hollowness. It can be seen from a comparison of data cited in Figures 5.15 and 5.16 that the relative strength of concretes containing cement with an increased slag content considerably exceeds this indicator for concretes containing cement with a slag content of up to 40% after steam curing and subsequent hardening. The data shown in Figure 5.16 on the increase in concrete strength upon steam curing indicate that for the concretes containing the cement under study with a 60-80% slag content, the length of isothermal curing need not be longer than 8 hours. Under short curing conditions, especially in low-grade concretes, the advantages of a cement containing 40% slag and pure neat cement become clear. By 28 days of subsequent hardening under normal conditions the strength of concretes steam cured under various conditions (Figure 5.16) equalizes to a considerable degree and hardly depends on the length of the isothermal period.

Thus, these studies have confirmed the advantages of using slag portland cement with a moderate slag content. These results show that concretes of average grades (200-300) can be obtained by utilizing the high activity of portland cement clinker and approximately 70% of the basic slag during thermal treatment.

When selecting cement for winter concreting it is necessary to consider the retarded hardening of cements with a high slag content, especially at low thermal treatment temperatures. In conjunction with this only quick-hardening slag portland cements which should contain no more than 30-50% slag and have a grade of at least 400 should be used in winter concreting of small-scale structures.



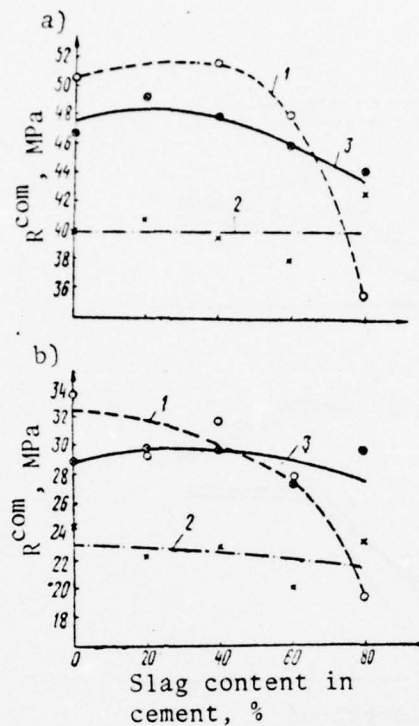


Figure 5.15. Change in Concrete Strength as a Function of Slag Content in the Cement Under Various Hardening Conditions. a,  $W/C = 0.4$ ; b,  $W/C = 0.6$ ; 1, 28 days of hardening under normal conditions; 2, Steam curing with a system 3 + 6 + 3 hours at  $t = 95^{\circ}\text{C}$ ; 3, The same, then 28 days of curing under normal conditions.

#### Requirements on Cements, Aggregates and Additives.

High strength quick-hardening concrete, grades 400-500 and higher, has been used more and more in recent years in construction. The technological aspects of making this concrete have still not been thoroughly treated in the literature and in instructional materials; this considerably hinders its successful introduction into large-scale construction with precast and cast in situ reinforced concrete. The use of this concrete is also of interest in winter concreting. The basic requirement for introducing high strength concrete is the production of quick-hardening high strength portland cements, crushed stone of hard rock, manufacture of stiff concrete mixtures with a low water-cement ratio and added workability substances with hardening accelerators.

Of the portland cements for manufacturing high strength quick-hardening concrete, it is most feasible to use high alite cements with a high content of one of the minerals fusing agents ( $C_3A$  or  $C_4AF$ ). High alite aluminate portland cements should be used for concretes which harden under natural conditions. Alite-alumoferrite portland cements are considerably more efficient for concrete subject to hygrothermal treatment.

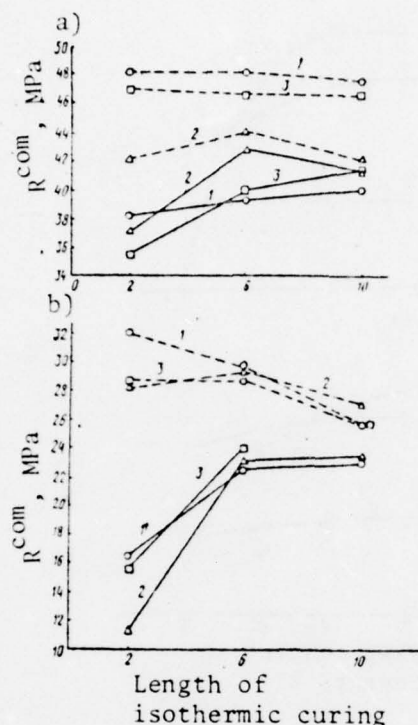


Figure 5.16. Change in the Strength of Concrete Containing Cements with a Varied Slag Content as a Function of the Length of Isothermal Curing at  $t = 95^\circ\text{C}$ . a,  $W/C = 0.4$ ; b,  $W/C = 0.6$ ; 1, Slag content 40%; 2, The same, 80%; 3, Without slag.. Solid lines show tests 10-12 hours after steam curing, dotted lines tests at age 28 days after steam curing.

The point of view that belite portland cements are advantageous for concretes subject to thermal treatment is valid only for long heating cycles which ensure the high relative strength of concrete, in particular when it is treated in an autoclave. Tests have shown that alite and high alite portland cements which comprise the main production of contemporary Soviet cement factories provide higher absolute strength of concrete under any hygrothermal treatment conditions, and a high relative strength for short-term heating (up to 12 hours).

The pulverization fineness of cement and the amount of gypsum added are of great importance in obtaining high concrete strengths at an early age of normal hardening and after thermal treatment. Tests were conducted on portland cements of widely varying mineralogical content to uncover the role of gypsum.

We ground the clinkers in a ball mill until 75% of the mass of the quantity taken would pass through a sieve with 10,000 holes/ $\text{cm}^2$ ; this corresponds approximately to the optimum specific surface of 4,000  $\text{cm}^2/\text{g}$ . During the grinding process 4% high strength semihydrated gypsum was added to the clinker. Granite gravel with a maximum particle size of approximately 30 mm and Moscow River sand were used as aggregates. The composition

of the concrete was 1:1:2.5 (by mass), the C/W = 2.78 (C = 500 kg/m<sup>3</sup>), the stiffness of the concrete mixture 25-30 s (slump of the standard cone 0). Before mixing additional gypsum was added to the cement to establish the optimum gypsum proportion. After molding some of the concrete samples were subjected to steam curing at 80°C for 17 hours, including 3 hours to raise the temperature (Table 5.9).

According to the indicators for 1 day and 3 day strength of normally hardening concrete, the optimum amount of semihydrous gypsum added is near 8% for low aluminate cement from the "Komsomolets" Factory (C<sub>3</sub>A - 2.91%), and for high aluminate cement from the Tauzskiy Factory (C<sub>3</sub>A - 17.07%).

As can be seen from the same Table 5.9, the presence of optimum gypsum content is especially important for the high aluminate cement from the Tauzskiy Factory, the strength of which drops when there is too much or too little gypsum. At the same time the change in strength of alite-alumoferrite cement was insignificant with the same variations in gypsum content.

The efficiency of thermal treatment of concrete containing alite-alumoferrite cement from the "Komsomolets" Factory was considerably higher with 4% gypsum added than in concrete containing the high aluminate cement of the Tauzskiy Factory. However, as the gypsum content in the latter increased the efficiency of steam curing the concrete increased significantly. The optimum amount of gypsum added for high aluminate cement is somewhat higher in a case of thermal treatment than when hardening under normal conditions. The question of the use of chemical additives is examined in more detail in Chapter 8; therefore we shall not dwell on it here.

TABLE 5.9. INCREASE IN CONCRETE STRENGTH DEPENDING ON GYPSUM CONTENT IN PORTLAND CEMENT AND HARDENING CONDITIONS

Portland cement	Addition, gypsum added, %	Total gypsum content, %	Compression strength limit							
			MPa				% of R <sub>28</sub> in the original cement			
			During normal hardening, at age, days			After steam curing	During normal hardening, at age, days			After steam curing
			1	3	28		1	3	28	
From the "Komsomolets" Factory	0	4	40,3	53,7	70	64,7	58	77	100	93
	2	6	44,9	59,8	—	64	64	85	—	92
	4	8	46,9	59,6	—	65	67	85	—	93
	6	10	40,7	56,2	—	64,9	58	80	—	93
From the Tauzskiy Factory	0	4	27,5	37,1	58	45,1	47	64	100	78
	2	6	37,1	39,9	—	49	64	69	—	84
	4	8	42,3	49,2	—	51,5	73	85	—	89
	6	10	20,7	42,5	—	52,3	36	73	—	90

Commas indicate decimal points.



Tests conducted on more than 20 cements have shown that efficiency of steam curing concrete containing modern cements is considerably greater than that standardized by former technical specifications at the time.

To obtain the greatest effect when working with mixed cements their composition is the most important factor, i.e., the ratio between clinker, gypsum and active mineral additive.

The activity of cement, as is well known, is determined by the amount of it used in concrete of a given strength and by placeability. Cement consumption as a function of its activity is shown in Figure 5.17 for concrete with a workable mixture corresponding to slumping of an average cone 2-4 cm. The curves on the graph show that to avoid great expenditures of cement it is feasible to use cements of grade 500-600 for high strength concrete (500 and greater) with a given placeability of the mixture.

More attention must be devoted the choice of the aggregates along with selecting the cements and designating the compositions of the concrete mixtures. Recent works have shown the feasibility of using light porous aggregates in cast in situ reinforced concrete. The use of sand-gravel mixtures is not permissible.

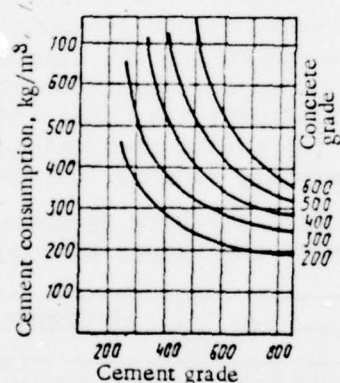


Figure 5.17. Dependency Between Cement Grade and Its Consumption in Concretes of Different Grades for Workability of the Concrete Mixture Corresponding to Slumping of a Standard Cone of 2-4 cm.

Six different types of coarse aggregate were compared in a specially conducted test: ordinary gravel; the same gravel, but crushed; crushed limestone; crushed granite; cement clinker (the most active coarse aggregate in a technical regard); crushed stone of dense magnetite. All other conditions being equal, from among the most widely used types of coarse aggregate the crushed granite provided the greatest strength to the concrete. With regard to the cement clinker gravel and crushed magnetite, compared to crushed granite they offered no advantage.

The strength of concrete drops 10-15% due to the weaker cohesion between the surface of the gravel grains and the mortar. Crushing the gravel, i.e., converting it to crushed stone (with a sufficiently dense rock and all other conditions being equal) increases concrete strength 10%.

Low workability mixtures with an increased and high cement consumption which are most characteristic for high strength concretes require a lesser sand content in the aggregate mixture. However, for each type of coarse aggregate (according to the shape and size of the grains and the grain composition) there exists a limit of reduction of coefficient  $r$  below which the mixture separates and loses its placeability regardless of its workability and cement content. The limit for reducing the relative sand content in an aggregate mixture (by mass) is  $r_{opt} = 0.25-0.28$ .

In addition to the strength of coarse aggregates, their resistance to freezing affects the strength of concrete in a number of cases. We studied the frost resistance of large aggregates for concrete for construction of the Kuybyshevskiy Hydroengineering Complex and for the Kamskaya Hydroelectric Station. In both cases crushed stone of igneous rocks (granite, diabase) and of sedimentary rocks (different types of limestones, dolomites) as well as gravel were tested. Frost resistance was tested for the Kuybyshevskiy Hydroengineering Complex up to 500 freezing and thawing cycles, and for the Kamskaya Hydroelectric Station up to 150 cycles. Crushed stone of particle size 50 and 150 mm was tested. The change in the mass of the crushed stone was established during the test. The mass of the crushed stone increased 0.2-1.2% up to 25 cycles due to additional saturation with water, and then by 75-150 cycles it dropped to the initial mass assumed to be 100. In all cases, except for porous limestone, samples of crushed stone from the North Caucasian Geological Administration sustained 500 freezing and thawing cycles. In doing this the limestone and dolomite lost approximately 2% of their mass, the granite and diabase less than 1%. Porous sand stone sustained 225 freezing and thawing cycles. Crushed stone of larger particle size lost somewhat more mass; this must be due mainly to mechanical actions in the process of loading the samples into the cold chamber and the water baths.

Tests have shown that igneous and dense sedimentary rocks have an extremely high degree of resistivity to freezing. Therefore, as a rule, it is not necessary to test dense rock, as is often required, up to 25-50 freezing and thawing cycles. These conclusions are also well confirmed by the results of tests of crushed stone samples supplied from the Kamskaya Hydroelectric Station site. Samples of igneous rocks (granite and diabase) as well as dense crystalline limestone sustained 150 freezing and thawing cycles. Samples of low-strength grade limestone sustained up to 50 freezing and thawing cycles. After 50 freezing cycles this limestone demonstrated considerable mass losses. By 100 cycles of the test many samples were destroyed, i.e., did not pass the frost resistance test. As a rule, limestone aggregates must be tested for frost resistance in concrete or the volumetric mass and porosity must be noted. Porous aggregates used to make light concretes, especially lightweight aggregate concrete has a relatively high resistance to frost.

Tests conducted by G. A. Arobelidze and V. I. Soroker in the laboratory of the Central Scientific Research Institute of Industrial Structures with workable, low workability and stiff mixtures have shown that when the cement consumption is increased from 200 to 800 kg/m<sup>3</sup> and optimum grain composition of the aggregate mixture for each cement input is ensured in doing this, the water requirement of a cement mixture of given placeability first drops somewhat or remains practically constant (approximately  $C = 400 \text{ kg/m}^3$ ), and then increases sharply. In this segment, in which the water requirement drops or remains practically constant, an increase in cement consumption leads to a reduction in the water-cement ratio and the corresponding increase in the concrete strength. On this same segment, in which the water requirement of the cement mixture increases when the cement consumption increases, a reduction in the water-cement ratio first has little effect, and then the increase in strength almost ceases. Thus, an increase in cement consumption above a certain limit is not accompanied by an increase in concrete strength. This limit depends on the placeability of the concrete mixture.

#### Comparison of the Physical-Mechanical Properties of Light Concretes Subjected to Thermal Treatment.

Thermal treatment is the most efficient method of accelerating the hardening of normal as well as light (containing porous aggregates) concretes. All other methods (increasing the activity of the cement, decreasing the W/C, introducing chemical additives and increasing the stiffness, consolidating the mixture) are used as additional measures which accelerate the concrete hardening processes in modern scales and rates of producing concrete and reinforced concrete building elements.

The great advantage of thermal treatment under factory conditions consists in that the industrial process for manufacturing structural elements does not depend on climatic conditions. In the USSR, as in all other countries, elements and structures of normal and light concretes as a rule are subjected to thermal treatment with steam at 70-95°C.

In recent years structures of various types of concrete have been undergoing electrical thermal treatment at the building sites as well as in the factories, and the concrete mixtures are first heated by an electrical current or steam.

The use of light concretes containing natural and artificial porous aggregates is continually growing compared to that of normal concretes. ^

In the Soviet Union almost 50% of the light concretes go for the manufacture of building elements and structures of lightweight aggregate concrete, the nomenclature of which is broad: concrete of grades 50 to 500 are used in it.

Tests were conducted in the laboratory for methods of accelerating concrete hardening of the Scientific Research Institute of Concrete and Reinforced Concrete to study the effect of the most widely used types of



thermal treatment on the physical-mechanical properties of lightweight aggregate cement. Lightweight aggregate cement of various grades was steam cured, subjected to electrical heating, autoclave treatment and was cured under standard conditions. The curing conditions were accepted as optimum for each type of treatment. In steam curing and autoclave treatment some of the samples were cured in hot water at the same time. In this case the samples were immersed in water in open forms 0.5-1 hour after preparation. Thermal treatment of the samples in all tests was carried out in metal forms which were open overhead. The treatment conditions are shown in Table 5.10. After thermal treatment the samples were tested at age 1-3 days from the instant of preparation and after storage for 28, 90 and 360 days under dry air conditions ( $W = 50-65\%$ ), in a standard chamber ( $W = 95-98\%$ ) and in water. The compression strength was determined in  $10 \times 10 \times 10$  cm cubes, the prism strength and modulus of elasticity and elastic strength during bending in prisms  $10 \times 10 \times 40$  cm. The principal results of the tests are cited in Table 5.10.

The greatest compression strength of lightweight aggregate concrete is obtained after autoclave treatment in a steam atmosphere and in water at  $174^\circ\text{C}$ . After steam curing it was approximately 85%, and under the same curing conditions in water 75% of 28 day normal hardening. The lowest strength of lightweight aggregate concrete is obtained after electrical heating. The strength of samples heated in water was lower than in those heated by steam under the same conditions due to destructive processes (capillary absorption of moisture during the development of contraction phenomena) which developed after immersing it in water.

It should be noted that the kinetics of gaining compression strength in lightweight aggregate concrete of grades higher than 150 does not essentially differ from normal concrete during thermal treatment. Concrete subjected to steam curing and electrical heating acquires nearly its complete rated strength upon subsequent hardening in a normal hardening chamber for 28 days. The rate of strength increase of heated samples upon subsequent hardening under dry air conditions up to 28 days is more intensive than in water, and is later retarded. At age 1 year, regardless of the initial and subsequent hardening conditions, the strength of lightweight aggregate concrete was essentially the same. The exception is lightweight aggregate concrete subjected to electrical heating and stored then under dry air conditions; its strength was 78% of  $R_{28}$ .

The prism strength of lightweight aggregate concrete after thermal treatment is directly related to the cubic strength. The ratio of  $R_{pr}/R_{cube}$  of lightweight aggregate concrete of grades 150-250 is 0.7-1.05 at age 1 day (after heating). In samples heated in water this ratio is greater than in samples heated with steam at the same temperatures. Moreover, it has been established that as the mass volume of lightweight aggregate concrete decreases, just as in fine grain concretes, the ratio  $R_{pr}/R_{cube}$  increases and is always higher than in normal concrete. According to the results of the studies of the laboratory of light concretes of the Scientific Research Institute of Concrete and Reinforced Concrete which were carried

out in accordance within the design of Soviet-French scientific-technical cooperation, the prism strength of lightweight aggregate concrete of grades 300, 400 and 500 determined in samples  $15 \times 15 \times 60$  cm steam cured as well as hardened under normal conditions, was 0.81 compared with the cubic strength, and in prisms  $10 \times 10 \times 40$  cm 0.88.

TABLE 5.10. EFFECT OF VARIOUS TYPES OF THERMAL TREATMENT ON THE PROPERTIES OF LIGHTWEIGHT AGGREGATE CONCRETE (ACCORDING TO THE DATA OF M. V. RABOTINA)

Concrete	Type and conditions of thermal treatment	Sample age, days	R <sub>cube</sub> , MPa	R <sub>pr</sub> , MPa	R <sub>pr</sub> /R <sub>cube</sub>	E · 10 <sup>3</sup> , MPa
Composition № 1. γ = 1150 kg/m <sup>3</sup>	Steam curing 1+2+6+2 hrs. at 95°C	3 28	13 —	13.3 —	1.02 —	9.2 —
	Autoclave treatment 1+2+6+2 hrs. at 174°C	3 28	15.5 —	15.2 —	0.98 —	8.7 —
	Normal hardening	28	15.2	15.3	1	9.2
Composition № 2. γ = 1300 kg/m <sup>3</sup>	Steam curing 2+3+6+2 hrs. at 80°C	1 28	21 25.3	20.8 26.7	0.99 1.05	12.2 14.2
	Autoclave treatment 1+0.5+6+2 hrs.	1 28	29 29.8	22.4 28.1	0.78 0.94	10.9 12.5
	Electric heating 4+5+2 hrs. at 80°C	1 28	14.6 24.5	11.8 24.5	0.82 1	10.9 12.3
	Normal hardening	28	25	24.3	0.98	13.6
Composition № 3. γ = 1550 kg/m <sup>3</sup>	Steam curing 1+2+6+2 hrs. at 95°C	3 28	22.2 26	21.4 21.3	0.97 0.82	14.4 16.8
	Autoclave treatment 1+2+6+2 hrs. at 174°C	3 28	34.3 33.7	30.9 31	0.9 0.92	15.8 17.9
	Normal hardening	28	26.2	22.2	0.85	16.4

Commas indicate decimal points.

In generalizing research conducted at different times, we may conclude that the ratio of prism strength to cubic strength for structural lightweight aggregate concrete regardless of the type of thermal treatment should be assumed to be 0.85. These values increase as the concrete grade and volumetric mass decrease.

With regard to the theory of strength, it may be noted that in spite of high adhesion properties (due to superior linkage of the haydite to the cement mortar), lightweight aggregate [haydite] concrete breaks down due to transverse separation. It begins after the haydite has reached maximum deformation.

The tensile strength of lightweight aggregate concrete during bending after steam curing and autoclave treatment matched the indices of normally hardened concrete by age 28 days. It was somewhat below the rated strength in lightweight aggregate concrete subjected to electrical heating. It should be noted that in samples heated in water at 80 and 174°C, the strength  $R_t^b$  is greater than in samples heated in a steam medium. Subsequent hardening in water also increases the tensile bending strength of samples. This indicates an increase in tensile deformability of lightweight aggregate concrete in a water saturated state. When samples are cured in steel forms, no significant splitting action occurred when water was absorbed by contraction phenomena in the lower layer of the concrete exposed to bending.

It must be kept in mind that storage of lightweight aggregate concrete under dry air conditions leads to a temporary drop in tensile bending strength. By age 1 year the increasing strength approaches that of concrete hardened under normal conditions, but is below that of concrete hardened in water. Testing of prisms of lightweight aggregate concrete of grades 300, 400 and 500 have shown that the ratio of bending strength to cubic strength after steam curing is higher than in that hardened under normal conditions for the entire time. This may be due to the superior cohesion of the mortar skeleton to the haydite granules during steam curing. In doing this hydraulic properties and a rough surface are manifested.

Studies of the deformation properties of lightweight aggregate concrete hardened under different temperature-moisture conditions are of special interest. The modulus of elasticity of lightweight aggregate concrete of various grades: 75-100; 150; 250; 300; 400 and 500 were studied at the Scientific Research Institute of Concrete and Reinforced Concrete in the laboratory of methods for accelerating the hardening of concrete and the laboratory of light concretes and light concrete structures. In this case the haydite was used with a varied volumetric mass, and quartz sand and sand produced by grinding haydite into granules was used as a fine aggregate. The moduli were determined at a stress of  $R = 0.2$  of the prism  $R$ . The results of determining the modulus of elasticity of samples made from lightweight aggregate concrete of grades 100-500 are cited in Table 5.11.

At age 1 day the modulus of elasticity of lightweight aggregate concrete subjected to all types of thermal treatment under the most



common conditions is 80-90% of the modulus of elasticity of the same concrete hardened 28 days under normal conditions. Subsequently the values of the modulus of elasticity increase. The modulus of elasticity is lower in lightweight aggregate concrete subjected to electrical heating; this corresponds to a reduced compression strength indicator. In doing this it should be noted that by age 360 days the modulus values are generally lower in a number of cases compared to age 90 days. A similar phenomenon is observed in normal concretes under dry air as well as water storage.

TABLE 5.11. VALUES OF THE MODULUS OF ELASTICITY OF CONCRETES SUBJECTED TO VARIOUS TYPES OF THERMAL TREATMENT (IN PRISMS 10 x 10 x 40 cm)

Concrete	Concrete grade	Initial standard modulus of elasticity, MPa	Normally hardened concretes		Concrete steam cured in a 2+6-2 hr. system at 90°C		Concretes electrically heated in a 2+6+2 hr. system at 90°C		Concretes subjected to autoclave treatment in a 2+6+2 hr. system at 0.9 MPa	
			E, MPa	% deviation	E, MPa	% deviation	E, MPa	% deviat.	E, MPa	% deviation
Containing Dubrovskiy haydite and haydite sand	200	15 000	—	—	14 370	-4,2	14 800	-1,3	—	—
	250	16 500	16 370	-0,8	16 800	+1,8*	—	—	—	—
	300	18 000	17 300	-3,9**	17 000	-5,5**	—	—	15 800	-12
Containing Lianozovskiy haydite and haydite sand	100	8 000	—	—	9220	+15,2	7830	-2,1	—	—
	150	10 000	9200	-8	—	—	—	—	8670	-13,3
Containing Volgogradskiy haydite and quartz sand	400	20 000	22 800	+14	19 500	-2,5	—	—	—	—
	500	23 000	—	—	22 600	-2	—	—	—	—
Normal containing dense aggregates	150	23 000	—	—	14 500	-36,8	18 450	-19,8	—	—
	200	26 500	31 300	+18	23 800	-10*	—	—	20 100	-36
	300	31 500	—	—	—	—	—	—	22 650	-25

\* Prisms tested at age 28 days after heating.

\*\* The same, at age 90 days.

After autoclave treatment, high-strength low alkaline calcium hydro-silicates of the tobermorite type are formed by the interaction of the clinker minerals with the ground quartz sand and haydite; these hydro-silicates lead to a 1.2 time increase in concrete compression strength compared to the 28 day strength of normal hardening. However, the change in the structure of the hydration products which leads to an increase in crystalline phase content due to the reduction in the gel-like structure and enlargement of the crystals themselves as well as reduced concrete moisture leads to a drop in its modulus of elasticity to 80% of the rated  $E_{28}$ . This is apparently associated with crystallization processes in the phase composition of new formations and the appearance of microcracks as the result of the inherent stresses arising in the concretes. We may conclude that by age 28 days the modulus of elasticity approaches 100% in steam cured samples stored under normal conditions, and in those subjected to electrical heating, it is 90% of  $E_{28}$ .

It should be noted in other studies a clear 20% drop in the modulus of elasticity is noted after steam curing grades 300-500 lightweight aggregate concrete compared to normally hardened samples. In a case of autoclave treatment the moduli of elasticity of lightweight aggregate concrete in the data cited were 15% lower, and in normal concrete even higher -- 20-35%.

Increased humidity of the medium exerts a positive time effect on the modulus of elasticity. We have established that by age 1-2 years the moduli of elasticity of not only light concretes but normal concretes may drop in a number of cases under constant storage conditions. The modulus of elasticity of lightweight aggregate concrete stabilizes after 1.5-2 years. As is apparent from these data, in the design and planning of structures of light concretes, not only the drop in the modulus of elasticity compared to normal concretes of the same grades, but also that in the various types of thermal treatment of them must be taken into consideration.

Standard moduli of elasticity established until recently depending on the volumetric mass of the coarse porous aggregate do not completely consider the role of the mortar component. The modulus of elasticity of light concretes depends on the elastic characteristics of the mortar component as well as that of the porous aggregates with a reduced modulus of elasticity. When loading these concretes the stresses and deformations are redistributed in the mortar and aggregate in working together. Since fewer defects are formed in the contact zone between the mortar and large aggregate, the resistance of lightweight aggregate concrete to cracking increases.

Measurements of overall and plastic deformations at  $R_{pr}$  0.4 and 0.8 have shown that up to age 360 days normally hardened samples have the least values of overall and elastic deformations, somewhat greater in steam cured and electrically heated samples and greatest in samples subjected to autoclave hardening. At age 1 day, i.e., soon after heating, the least plastic deformations are obtained in lightweight aggregate concrete subjected to autoclave hardening, and the greatest in that electrically heated. Consequently, considerable structural disturbances occur in concrete during electrical heating due to the directional effect of the capillaries and moisture gradients. A reduction in plastic deformation is observed later. During water storage these values are somewhat greater than in dry air storage.

It is interesting to note that samples of high strength dense lightweight aggregate concrete did not let water pass at all in testing for water permeability up to 0.12 MPa. This is promoted by swelling of the porous aggregates and the density in the contact zone. A structure of steam cured samples was more dense than that of those hardened under normal conditions for the entire time. Studies show that the water permeability of normal concretes also increases after steam curing under mild conditions.

G. P. Kurasov of the laboratory of light concretes tested lightweight aggregate concrete of grades 200-400 for standard resistance to freezing in approximately 300 freezing and thawing cycles. The results of the tests are shown in Table 5.12.

All the compositions tested were quite resistant to freezing. Coefficients of frost resistance greater than 1 were obtained everywhere, i.e., the strength indices of control samples were smaller than in those subjected to freezing and thawing 100, 200 and 300 cycles. Excesses in the strength of concrete samples subjected to freezing were from 1 to 16%. A coefficient of 0.96 was obtained only in one case after 200 freezing cycles in normally hardened concrete of grade 400. A high resistivity of lightweight concretes containing coarse aggregates to freezing was also observed in other cases. In contrast to normal concretes thermal treatment does not result in a drop in the resistivity of lightweight aggregate concrete to freezing. The use of dense aggregates in many cases adversely affects the mechanical properties of concrete, overworking the mortar skeleton which is without good contact with the coarse aggregate.

TABLE 5.12. RESULTS OF TESTING THE RESISTIVITY OF LIGHTWEIGHT AGGREGATE CONCRETE TO FREEZING

Compression strength limit of water saturated samples before the beginning of freezing, MPa	Number of freezing and thawing cycles								
	100			200			300		
	Compression strength limit, MPa		Coefficient of resistivity to freezing	Compression strength limit, MPa		Coefficient of resistivity to freezing	Compression strength limit, MPa		Coefficient of resistivity to freezing
	After freezing	Of control samples		After freezing	Of control samples		After freezing	Of control samples	
20,8 (Steam cured)	27,4	24,1	1,13	29,8	25,7	1,16	28,9	27,9	1,03
33,3 "	42,2	38,7	1,09	40,2	36,5	1,10	44,9	38,8	1,16
38,3 (Not steam cured)	38,5	38,2	1,01	39,3	41	0,96	48,3	44	1,1
40 (Steam cured)	39,9	36,6	1,09	45	41,2	1,09	46,7	44,5	1,05

Commas indicate decimal points.

Thus our studies have shown that, except for the modulus of elasticity (where the overall density and mass play a greater role), all indicators of the physical-mechanical properties of lightweight aggregate concrete are high enough. This type of concrete may be recommended for wide usage not only in factory manufacture of articles with thermal treatment, but in cast in situ structures as well, including during winter concreting. Lightweight aggregate concrete is highly resistant to freezing and due to



the porosity of the aggregates is less subject to harmful actions during early freezing than normal concrete containing dense aggregates. In conjunction with the increased water retaining ability lightweight concretes should be used more widely when concreting under dry and hot climatic conditions. All this justifies in many cases the recommendation that lightweight aggregate concrete and other lightweight concretes are preferable to normal concrete.

#### Recommended Conditions for Thermal Treatment of Concrete.

In most cases various methods of thermal treatment of structures (electric thermal treatment, steam curing, air heating) are used under winter conditions to accelerate concrete hardening. Under site conditions it is even more difficult than under factory conditions to obtain the concrete grade required by the plan without consuming too much cement. The concrete strength standardized at age 28 days or at other periods at which the structure sustains the entire design load is called the design grade. The design grade of the concrete is indicated in the plans of buildings and facilities and in the plans of operational organization. The operating methods used should guarantee that the design strength of the concrete be achieved in indicated periods, regardless of hardening conditions. The permissible dismantling strength is indicated in percentages of the design grade of the concrete in the structures.

The thermal treatment conditions of the structures should be designated with consideration of the minimum cement consumption and expenditure of energy resources to provide the required concrete quality. In electrical heating this is done using higher curing temperatures (up to 80°C) at the isothermic level. Practice shows that it is difficult to maintain the temperature higher than at the 40-50°C level when steam curing in steam jackets. The temperature remains even lower when using heaters or steam in winter shelters.

Thermal treatment of concrete in cast in situ structures is more efficient up to the time it obtains a strength of 50-70% of  $R_{28}$ . The following measures are recommended to produce 70% of the strength immediately after heating: use concrete mixtures with a W/C no more than 0.5; prepare concrete containing highly active or quick-hardening cements; introduce additives into the concrete mixture -- hardening accelerators.

To produce 100% strength in the concrete immediately after heating it is necessary to increase cement consumption or lengthen the isothermic heating time (for example, for concretes containing slag portland cement).

Thermal processing conditions are selected to ensure the required strength of the concrete depending on the type and activity of the cement, concrete composition, type of structure to be heated and other factors. At the same isothermic heating temperature the duration of heating concrete containing slag portland cement should be increased in comparison to the duration of heating concrete containing portland cement. Therefore in order to shorten the overall heating time of concrete containing slag portland

cement it is recommended that the temperature for isothermic heating of it be increased to 90-95°C.

To reduce the consumption of fuel and electrical energy it is necessary to try to obtain the required concrete strength in the shortest heating time. For this reason it is recommended that the maximum allowable temperature be used, the duration of active heating be shortened by considering the increase in concrete strength during cooling, quick-hardening cements used, and other methods of accelerating concrete hardening employed in the complex. At the present time at winter sites builders warm up and heat concrete in structures mainly by using electrical energy.

Depending on a number of factors and methods used, heating is carried out in different ways:

a) isothermic curing and raising the temperature. In this method the required concrete strength should be achieved by the time isothermic heating is completed, and the increase in strength during cooling is not considered. This method should be used when electrically heating structures with a surface modulus  $M_s = 12$  and above;

b) raising the temperature, isothermic heating and cooling. In this system concrete acquires the necessary strength by the end of cooling. The use of this system is feasible for heating structures with a  $M_s = 7-10$ . During heating it is feasible to disconnect the electrical current for some time to reduce desiccation and increase the electrical conductivity of the concrete;

c) raising the temperature and cooling. In this case a set strength is ensured by the end of cooling. The use of this system is recommended for structures with a surface modulus of 6 and less;

d) a gradual method in which the concrete is heated first, for example, up to 50°C and maintained at this level for 1-3 hours, then the temperature is raised more rapidly to the maximum allowable for a given structure and held there until the concrete acquires the necessary strength.

When using concrete mixtures preheated with an electrical current or steam the concrete in the form-work may be cured using the thermos method or in heated form-work. The use of the latter is especially feasible when conducting operations at low sub-zero temperatures. In the electrode method of heating in some cases a self-regulating system is used in which the voltage in the circuit remains constant for the entire thermal treatment cycle, i.e., the concrete is heated at one transformer voltage stage.

In the self-regulating system the change in the temperature in the body of the structure or part corresponds in nature to the change in the electrical conductivity of concrete during its hardening process. It is characteristic for this system that a certain maximum temperature distinctive to only a given rate of heating corresponds to each rate of temperature increase of the concrete in the actual structure. At some sites

and in some factories the thermal energy is not supplied constantly, but in discrete pulses which alternate with pauses. During the pause the heat and moisture is redistributed through the cross-section of the structure due to the thermal conductivity of the concrete; this ensures a more uniform temperature and moisture field. The voltage continues to be sent in pulses during the isothermic curing period as well. In this case the length of the pulse is shortened, and the period of pauses is lengthened compared to those in the heat-up stage. The length of the pulse and pauses depends on the set heat-up rate, the temperature of isothermic heating, the surface modulus of the structure, voltage input, etc., and should be established by testing. The use of self-regulating and pulse heating systems is recommended when there are no special transformers of the required power with smooth or step voltage regulation at the factory or site.

Precuring the concrete for 2-6 hours at a normal or low above-zero temperature down to 5°C before beginning heating has a positive effect on the quality of concrete subject to thermal treatment. The concrete cannot be precured at heating rates up to 10°C/hour.

As the rate of temperature increase rises as the result of the difference in the coefficient of linear and volumetric expansion of individual components of the concrete, the overall deformations (especially expansion) of the material increase considerably; these indicate that structural damages in it and a deterioration of its properties are occurring. To avoid defects in the structure, the concrete should be heated with a slow or gradual temperature rise.

In cast in situ structures the rate of temperature increase should not exceed the following when heating the concrete:

- 15°C/hour - for skeleton and thin wall structures at  $M_s = 10 \dots$   
... 12 and more, and for structures erected in a  
sliding casing
- 10°C/hour - for structures with a  $M_s = 6 \dots 9$
- 5-8°C/hour - for structures with a  $M_s = 3 \dots 5$ .

The duration of isothermic curing of concrete may be approximately fixed from the graphs shown in Figures 5.18-5.19. The graphs are compiled for concretes of mixtures with an initial workability of 2-4 cm slump.

Figure 5.18 shows curves of the strength increase of concrete of grades 200, 300, 400 and 500 containing grade 400 portland cement with consideration of 2 hour precuring before beginning heating, a 3-4 hour temperature rise to 80°C and at least a 4 hour cooling period after isothermic curing. The gain in concrete strength must be considered for this period.



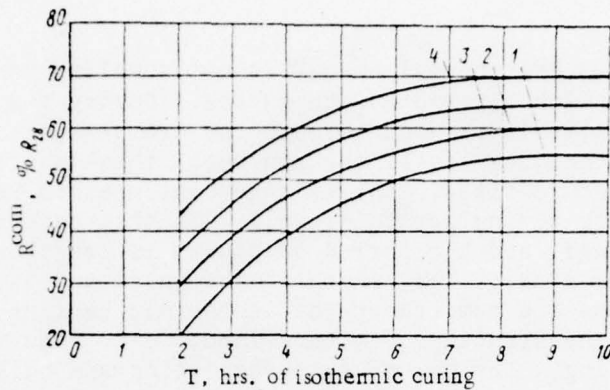


Figure 5.18. Intensity of the Strength Increase of Concrete of Various Grades Containing Portland Cement at a Temperature of Isothermic Heating  $80^{\circ}\text{C}$ . 1, Grade 200 concrete ( $\text{W/C} = 0.67 \dots 0.77$ ); 2, Grade 300 concrete ( $\text{W/C} = 0.5 \dots 0.59$ ); 3, Grade 400 concrete ( $\text{W/C} = 0.4 \dots 0.45$ ); 4, Grade 500 concrete ( $\text{W/C} = 0.33 \dots 0.36$ ).

Figure 5.19, a shows curves of the strength increase of grade 200 concrete containing grade 300-400 portland cement with consideration of the characteristics of the conditions cited in Figure 5.19.

On winter sites slag portland cements should be of grade 400-500. But, unfortunately, they are more often of grade 300.

Figure 5.19, b shows curves of the strength increase of grade 200 concrete containing grade 300 slag portland cement with consideration of the characteristics of the conditions cited in Figure 5.18.

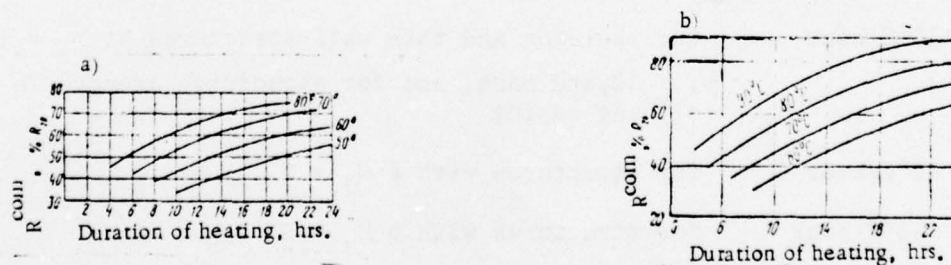


Figure 5.19. Intensity of the Strength Increase of Grade 200 Concrete at Various Isothermic Heating Temperatures. a, Containing portland cement; b, Containing slag portland cement.

Heating conditions identical to those for heating normal concrete should be assumed for grade 150 and higher structural lightweight aggregate concrete. The final heating conditions of the concrete in the structures is established by a building or factory laboratory from the results of experimental heating of concrete of a given composition containing the materials used. Thermal treatment of grade 100 and lower lightweight aggregate concrete, i.e., less dense, is more efficient.

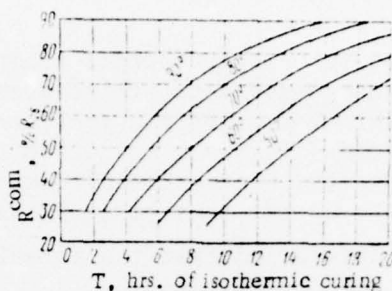


Figure 5.20. Intensity of the Strength Increase of Grades 50-100 Lightweight Aggregate Concrete Containing Portland Cement at Various Isothermic Heating Temperatures.

Figure 5.20 shows the curves of the strength increase of lightweight aggregate concrete of grades 50-100 containing grade 400 portland cement with consideration of the characteristics of the conditions cited in Figure 5.18. The harshness [stiffness] of the concrete mixture is assumed to be 30-40 s.

The efficiency of thermal treatment of lightweight concretes is greater the less their volumetric mass. The maximum temperature for thermal treatment of parts and structures of light concretes is ordinarily 90-95°C.

It is feasible to stop isothermic curing of large-size elements and structures 25-40 cm thick of light concrete when the concrete reaches approximately 50% of its rated strength, since hardening of the concrete continues during slow cooling after heating at an air temperature of 15-20°C, and its strength may reach 70-80%  $R_{28}$  in 8-12 hours. Steam insulation of an open concrete surface during heating is not required when thermally treating parts and structures of light concretes on which no requirements limiting final moisture are levied by corresponding technical specifications.

After heating is stopped at a strength of 50-70% of the rated strength, light concretes of grades up to 150 containing light sands (crushed haydite, agloporite, etc.) subsequently acquire 100-110% of the rated strength after 28 days hardening under favorable hygrothermal conditions.

Thermal treatment of prestressed reinforced concrete structures should be carried out only gradually to avoid disrupting the cohesion of the concretes to the reinforcement metal and to avoid possible considerable losses in the preliminary stress of the reinforcement metal. Isothermic heating should be conducted if possible at the maximum allowable temperature.

The maximum temperature for isothermic heating with concrete in structures with a  $M_s < 3$  (blocks of hydrotechnical facilities, foundations under equipment, etc.) is established with consideration of the formation of a temperature field which would ensure a favorable thermally stressed state of the structure during its hardening process. This is achieved by any methods which ensure that a uniform temperature is maintained throughout the cross-section of the block.

The maximum temperature for electrothermal treatment of reinforced concrete structures with prestressed metal reinforcement should be fixed with consideration of possible losses of the preliminary stressing of the metal reinforcement. Stress losses  $\sigma$  are directly proportional to the temperature difference of the heated concrete and metal reinforcement  $t_1$  and supports  $t_2$  which take up the tensile stresses of the metal reinforcement; they can be determined from the formula  $\sigma = 20 (t_1 - t_2)$ . Stress losses of the metal reinforcement during heating should be considered when designing the structure.

Thermal treatment of cast in situ skeleton constructions and frameworks with rigid fixing of multiple joints should be carried out, as a rule, at a temperature of isothermic concrete heating no higher than 40°C to avoid the occurrence of large temperature stresses and the appearance of cracks.

Attempts should be made to reduce temperature drops in different cross-sections of the structure during the entire thermal treatment process to ensure uniform concrete strength in all parts of the heated structure and to reduce temperature stresses. For this purpose it is necessary to provide thermal insulation of heated parts and structures, especially their individual parts which are subject to rapid cooling (angles, protruding parts).

To prevent the appearance of cracks in structures the temperature drop between the open surface of the concrete and outside air should not exceed: 20°C at  $M_s$  from 2 to 5; 30°C at  $M_s$  5 and above.

Unjacketed surfaces of structures and parts must be protected from water evaporation during thermal treatment to avoid overdrying the cement (primarily of the surface layers) and the deterioration of its properties associated with this. This may be done by carefully covering them with steam insulating materials (polymer layer, rubberized fabric, rubberoid, etc.) with installation of thermal insulation above it if necessary.

The intensity of cooling of cast in situ structures should correspond to the requirements of SNiP [construction norms and regulations] III-V. 1-70 by the end of electrothermal treatment and should be taken from Table 5.13.

Thin elements, angles and projecting parts which cool more rapidly the main structure should be insulated or heated in addition to ensure uniform cooling conditions of the parts of the structure which differ in thickness. The dimensions of a section with increased heating should be specified by the operational plan. Heating units should be installed and thermal form-work prepared in such a manner that a uniform temperature field is provided in the structures being concreted.



TABLE 5.13. ALLOWABLE RATE OF STRUCTURAL COOLING

Structure being concreted	Surface modulus of the structure, $m^{-1}$	Allowable curing rate, $^{\circ}C/hour$
Weakly reinforced concrete	15-10	12
The same	9-6	5
"	5-3	2-3
Medium and strongly reinforced concrete	8-15	No more than 15

#### Concrete Permeability and Frost Resistance.

Practice has shown in studies have confirmed that concrete and reinforced concrete structures and facilities are most severely damaged by their repeated freezing in a water-saturated state.

The intensity of damage (physical corrosion) depends on the density and nature of the porosity, hardening conditions, gain in strength, as well as the concrete age before the beginning of cyclical freezing and thawing.

Concrete in hydrotechnical, roadway, airport, irrigation and other facilities subject to repeated freezing and thawing are especially subject to severe destructive effects. These harmful effects on concrete are amplified under several climatic conditions due to low sub-zero temperatures, in regions in which the temperature frequently passes through  $0^{\circ}C$ , when it is saturated by aqueous saline solutions. The mechanism of the destructive action is associated with the phase transformation of water into ice and the crystallization of salts out of solution in the case of drying within the concrete pores.

Many authors explain the damage by the hydraulic pressure of the water squeezed out by the ice, the crystallization pressure of ice and salts, the special nature of the segregation of ice in micropores and capillaries, formation of ice lenses as the concrete freezes layer by layer and other causes.

The external indication of concrete destruction is the volumetric increase as the result of its expansion during freezing and saturation as well as due to compression during thawing and drying. In this case a system of micro- and macrocracks is formed and inherent structural tensile stresses arise.

In contrast to homogenous stone materials, concrete as a conglomerate material contains aggregates and cement stone with various moduli of elasticity. Along with pore structure, this is also the basic factor affecting frost resistance. The coefficients of temperature expansion of the concrete components are different.

Rapid destruction of concrete and stone facilities subject to the action of the low sub-zero temperatures of northern climatic conditions may be observed in the regions of Magadan and Yakutsk, and the effect of a temperature frequently passing through  $0^{\circ}\text{C}$  in the region of Murmansk. As examples of good preservation of structures built hundreds and thousands of years ago under the dry climatic conditions of the south, we may cite the pyramids of Cheops, Chephren, and Mencuar which were erected more than 4,000 years ago in Egypt. Limestone blocks weigh 2.5 tons each have been well-preserved up to the present. The same can be said about the state of preservation of very large blocks in Baalbek (Lebanon), columns in the City of Palmyra, etc. Many buildings and port facilities built tens and hundreds of years ago can be observed in a well-preserved state due to the dry and moderately cold climate of Central Asia (Samarkand, Bukhara), the Caucasus (cities of Armenia, Georgia) and the Crimea (Kherones, Feodosiya). Water pipes and viaducts built at the beginning of our era and in the Middle Ages using concrete containing limestone-pozzuolanic cements remain well preserved up to the present in Italy, France, Spain. In the burial chambers of Tutankhamun (Egypt) built more than 3.5 thousand years ago, 150 objects have been preserved without apparent damage, including such articles as a gypsum vase with artistically executed drawings. All materials are well preserved and durable without a change in temperature and humidity, i.e., under steady conditions. Under these conditions concrete is a sturdy and durable material.

The frost resistance of concretes as well as their strength depend to a considerable degree on the quality of the materials used and the formation of the appropriate structure. Additives play an important role in imparting concrete structural strength and durability. The better the quality of the material, the less of it may be consumed to erect structures in manufactured parts with the same supportive power and durability. Thus, for example, such alloying elements as nickel, molybdenum, silicon, chrome, manganese, and vanadium are included in steel to improve its physical-mechanical properties. Alloying elements increase the strength of carbon steel 20-40%, impart it the property of increased resistance to cold, which is very important when using it at low sub-zero temperatures. Alloying elements improve casting properties, weldability, etc. By now this has become daily practice in the steel casting industry. In exactly the same manner the manufacture of concrete with various chemical and certain mineral additives should become customary. By introducing a varied class of additives it is possible to improve the properties of concrete mixtures, control concrete setting and hardening times, and increase the physical-mechanical properties and durability of it in structures and facilities.

In spite of the great urgency of the problem, methods for determining resistivity to freezing have been inadequately cultivated both here and abroad and require improvement. Such methods must be developed which may reduce the time and difficulty of testing concrete for resistivity to freezing.

At present accelerated test methods using expansion deformation (All Union Scientific Research Institute of Transportation Construction of the

Ministry for Transportation Construction) and by freezing at  $t = -50^{\circ}\text{C}$  instead of  $t = -15 \dots -20^{\circ}\text{C}$  (Scientific Research Department of the S. Ya. Zhuk All Union Planning, Surveying and Scientific Research Institute) are permitted in the GOST [All Union State Standard] developed for operative checking of concrete frost resistance. A direct dependency between deformation and the degree of frost resistance is not always observed in deformation testing since some concretes exhibit spontaneous slumping associated with the structure of the concrete and aggregates. In freezing tests at an ambient temperature of  $-50^{\circ}\text{C}$  and up to 200 cycles the ratio of results is 1:10, but by 500 cycles this ratio changes to 1:5. In this case an overall picture of the relative resistivity to freezing of concrete and aggregates becomes greater. Concretes containing pozzuolanic portland cement are destroyed first, then those containing slag portland cement, and finally, those containing portland cements depending on mineralogical composition and activity.

Of the dense aggregates, crushed limestone and sandstone are destroyed first depending on their quality, and then crushed igneous rock (granite, diabase).

In developing this accelerated method the results were compared for concretes containing materials of varying quality, including those with workability and air entraining agents added to the mixture. Therefore many compositions, in accordance with the standard, sustained up to 600 freezing cycles.

Tests of resistivity to freezing using the change in the dynamic modulus of elasticity of concrete prisms have been conducted by foreign as well as Soviet researchers. In foreign practice this method is rather widely used in testing concrete for resistivity to freezing. The criteria for estimating frost resistance are usually assumed to be: a 25% loss in strength of cubes or cylinders, weight loss approximately 5%, expansion deformation up to 1 mm/m, change in the external appearance of the samples on a scale of 10. All these methods yield comparable results in terms of achieving under laboratory conditions some degree of material durability relative to high results. However, it is not possible to convert to concrete durability under large-scale conditions from the results obtained. The dependencies between laboratory tests of the frost resistance of concrete, cements and aggregates on the one hand, and the operating conditions of facilities under large-scale conditions are too complex. This is due to the diversity of climatic conditions, difference in concrete behavior in laboratory samples and in structures of varying massiveness, the aggressivity of the atmosphere and other factors.

At the First Symposium on Winter Concreting in 1956 speakers from Sweden noted that the temperature passes through 0 sixty times a year in the southern part of their country, where most of the construction is carried out. The maximum total temperature drop in doing this does not exceed  $15^{\circ}\text{C}$ . Therefore they have found it necessary to freeze concrete samples at  $-10^{\circ}\text{C}$  in testing for frost resistance. A temperature of  $-40^{\circ}\text{C}$  which sometimes occurs in the northernmost parts of Sweden is recommended for a single freezing test.



A. Vellmi (Switzerland), who talked on measures to achieve high quality concrete under winter conditions, noted that in case of repeated freezings the concrete should have a strength of at least 15 MPa by this time, and the coefficient of saturations should be no greater than 0.9. In recommending the use of all measures to produce quick-hardening concrete, A. Vellmi proposed the use of sodium carbonate instead of calcium and sodium chlorides to avoid corroding the metal reinforcement.

The range of variation in sub-zero outside air temperatures and the number of transitions through  $0^{\circ}\text{C}$  are very great in our country. Table 5.14 gives the basic requirements of building standards for resistivity to freezing depending on the operating conditions of the structure.

Requirements for cements, aggregates and admixtures as well as for concrete compositions, manufacture technology, and mixture placement have been stated in a special handbook.

The author has conducted repeated tests on the frost resistance of concretes containing various cements and aggregates in the laboratory of concretes and cements of the Central Scientific Research Institute of Industrial Structures and at the All Union Scientific Research Institute for the Construction of Petroleum Industry Enterprises. Samples  $20 \times 20 \times 20$  cm containing 3 portland cements, 2 pozzuolanic portland cements, 2 sand-pozzuolanic portland cements, bauxite and gypsum-slag cements were tested for frost resistance in 1939-1941 on the building of the Central Laboratory of Construction Concretes of the Kuybyshevskiy Hydroengineering Complex (Table 5.15). In this case the samples were frozen for 12 hours in a cooling chamber at from  $-8$  to  $-22^{\circ}\text{C}$ . The samples were thawed in large water baths for 12 hours at  $10-20^{\circ}\text{C}$ .

TABLE 5.14. RATED GRADES OF CONCRETE IN TERMS OF FROST RESISTANCE FOR CONCRETE AND REINFORCED CONCRETE STRUCTURES, BUILDINGS AND FACILITIES OF CLASS 1 (EXCEPT FOR OUTSIDE ENCLOSURES)

Construction operating conditions	Required concrete grade in terms of frost resistance
Cyclical freezing and thawing in the water saturated state (above-ground parts of cooling towers, reservoirs, etc., and structures located on a seasonally thawing layer of permafrost soil).	300
Cyclical freezing and thawing under occasional water saturation conditions (structures constantly exposed to atmospheric activities).	200
Possible occasional effect of temperatures below $0^{\circ}\text{C}$ on structures in a water saturated state (structures in the ground or under water)	150
Possible occasional effect of temperatures below $0^{\circ}\text{C}$ under moist air conditions (internal structures of heated buildings and facilities during construction and assembly).	100

Note. According to SNiP 11-A.3-62, for the second, third and fourth classes of buildings and structures the required grade in terms of frost resistance drops one, two and three degrees respectively, but not below 50.

Coarse aggregates used consisted mainly of limestone and dolomites from the Kuybyshevskiy deposits. Crushed granite was used as the coarse aggregate in a number of series of concrete samples.

Concrete samples were tested for frost resistance up to their complete destruction at ages 7, 28, 90 and 300 days of normal hardening. During the testing process the samples were weighed before beginning and after saturating them with water, and also during the freezing process after 25, 50, 100, 200, 300, 400, 500 and 600 cycles; in this case some of the samples were tested for strength.

Figure 5.21 shows data of the variation in mass of concrete samples containing 2 portland cements (grades 400 and 500) with cement consumption from 250 to 400 kg/m<sup>3</sup> and samples containing crushed dolomitized limestone from the Shiryayevskiy deposit with approximately 4-5% water absorption. As can be seen from Figure 5.21, the mass of the samples increased 0.5-1% due to water absorption at first up to 10-15 freezing and thawing cycles. Later, the mass remained constant for up to 25 cycles and then began to decrease. By 150 freezing and thawing cycles the samples obtained the original mass. All the samples in this series sustained approximately 500 freezing and thawing cycles with a total mass loss of only 2-3%. In doing this the indicators for concrete containing grade 500 portland cement with a reduced W/C were somewhat better. In testing concretes containing various cements the frost resistance of the concrete containing sand-pozzuolanic portland cement at grade 400 and at concrete grade 250 was below 200 cycles at age 30 days. The frost resistance of concrete containing pozzuolanic portland cement was even lower. As can be seen from Figure 5.22, concrete containing pozzuolanic portland cement was completely destroyed by 400 cycles when the tests for frost resistance began at the same age in months. On the scale of 10 adopted by S. V. Schestoperov, concrete samples containing pozzuolanic portland cement dropped from 10 to 8 by external appearance by 200 cycles, then the samples are radically destroyed. Concrete containing portland cement presents a completely different picture. In testing at the same age in months the rating of the concrete samples dropped from 10 to 8 by external appearance only after 375 freezing and thawing cycles. As is apparent from Figure 5.22 and other data, destruction begins considerably earlier in samples tested at age 7 days. This should be especially emphasized for cases of use of low active and pozzuolanicized cements; consequently, the frost resistance of concrete increases considerably as the concrete strength rises at the beginning of the test. The satisfactory state of concrete in such dams as the Volkhovskaya and Dneprovskaya 40 and 50 years old confirms this assumption.

As is apparent from these graphs, the segment which characterizes, as it were, the limit or degree of concrete frost resistance can be determined from the variation in the curves. After the resistance of the concrete to the cyclical action of water and frost reaches a certain limit, intense destruction of it sets in.

TABLE 5.15. CHARACTERISTICS OF CEMENTS USED IN TESTING CONCRETES FOR FROST RESISTANCE

Cement	Mineralogical composition				
	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>3</sub> A	C <sub>3</sub> AF	C <sub>4</sub> SO <sub>3</sub>
Grade 500 portland cement from the "Red October" Factory.	61,5	15	5	15	1,5
Grade 400 portland cement from the Kramatorskiy Fact.	48	28	8	11,4	2,2
Grade 300 portland cement	47	31	6	11	2
Grade 500 high alumina cement from the Pashiyskiy Factory.	—	—	—	—	—
Grade 300 gypsum-slag cement from the Kharkovski Grinding Installation	—	—	—	—	—

Note. Pozzuolanic portland cement is obtained by adding 30% tripoli to the portland cement from the "Red October" Factory, and sand-pozzuolanic portland cement by adding to the same portland cement ground sand and tripoli together in an amount of not more than 50%.

Commas indicate decimal points.

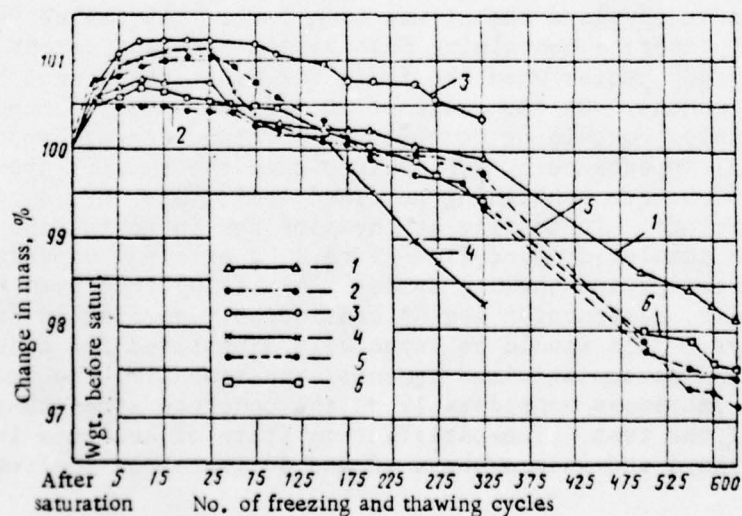


Figure 5.21. Change in Mass of Concrete Samples During a Test for Frost Resistance.



Position	Concrete grade	Consumption	
		Cement	Water
1	500	300	195
2	500	250	300
3	500	300	180
4	500	277	180
5	500	400	214,5
6	500	400	195

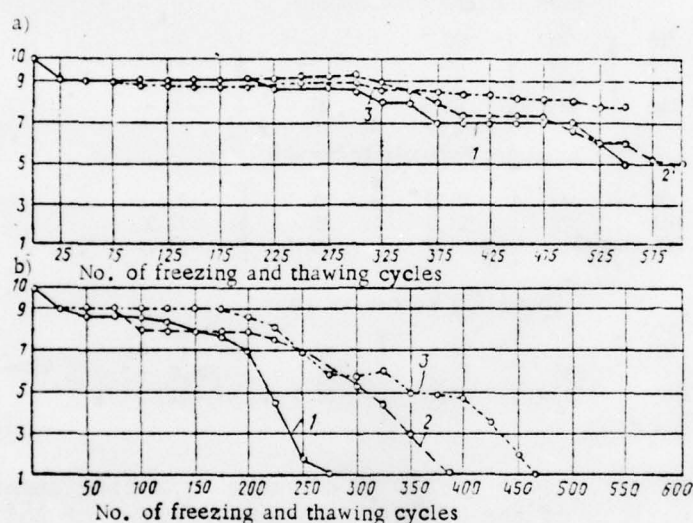


Figure 5.22. Curves of the Rating of Frost Resistance of Concrete Samples Composed of: a, Portland Cement and b, Pozzuolanic Portland Cement by External Appearance. Age of the samples: 1, 7 days; 2, 28 days; 3, 300 days.

Table 5.16 gives the results of tests for frost resistance of concrete samples  $20 \times 20 \times 20$  cm produced by vibration using 3 different cements.

Tests have shown that portland cement is the most frost resistant of the cements. Somewhat poorer results are shown by bauxite cement produced by blast furnace fusion. Pozzuolanicized portland cements exhibit somewhat less on frost resistance.

As is apparent from Table 5.16 portland cements containing 47-61% tricalcium silicate and 5-8% tricalcium aluminate were used in these tests. These types of cements were completely frost resistant, as can be seen from the results obtained. In other tests portland cements with a higher  $C_3A$  content exhibited reduced frost resistance and even water resistance.

In contrast to pure bauxite cements, sulfated bauxite cements also exhibit reduced frost resistance.

TABLE 5.16. CHANGE IN STRENGTH OF CONCRETE CONTAINING VARIOUS CEMENTS IN TESTING FOR FROST RESISTANCE

Sample age before freezing	No. of test cycles	Actual sample age, days	Strength after test, MPa	Strength of standard samples at an equiv. age	Strength change, %
Containing portland cement					
28	25	41	20.7	—	—
28	100	67	26	—	—
28	200	168	28.4	34.4	-17.4
28	300	216	25.9	37	-30
Containing Pozzuolanic cement					
28	25	43	21.2	22	-3.6
28	100	72	21.2	25	-15.2
28	200	215	7.1	29	-75
Containing bauxite cement					
90	25	111	59.3	62	-4
110	100	286	52.3	64	-18
110	200	287	50.7	64.5	-21

The reduced frost resistance of gypsum-bauxite expanding cement is noted in the specifications of the Ministry of the Industry of Building Materials of the USSR. This is due to the fact that the calcium sulfoaluminate formed during hardening is insufficiently frost resistant, and therefore cements of this type cannot be recommended for use in concretes of increased frost resistance.

Long-term tests conducted by us for 2.5 years demonstrated the role of concrete aggregates as well. In doing this it happened that concrete containing not only crushed igneous rocks, but also crushed limestone in dolomitized limestones has a high degree of frost resistance.

Dense concrete containing high quality portland cement sustains approximately 600 freezing and thawing cycles when using crushed limestone with approximately 4-5% water absorption as the coarse aggregate. When cements of higher activity are used and their grinding fineness is increased to within 95% passage through a sieve with 4900 holes/cm<sup>2</sup> (or approximately 4000 cm<sup>2</sup>/g) the resistance of concretes and mortars containing them rises.

As studies conducted by V. M. Medvedev and A. A. Gordeyev at the S. Ye. Zhuk All Union Planning, Surveying and Scientific Research Institute and by S. V. Shestoporov et al. at the Scientific Research Institute of Roads, the use of workability agents, in particular sulfite-alcohol distillery washes, significantly increases the frost resistance of concrete. At the same time it was established that the frost resistance of concrete in the presence of salts, especially manganese and ammonium sulfates, drops sharply.

An increase in the amount of sand in the concrete and a reduction in its grain size, and consequently an increase in the surface modulus of the sand, substantially lowers the technical properties of concrete. In these cases the frost resistance of concrete drops somewhat as the result of increasing cement and water consumption. As tests show, the use of air entraining additives to the concrete plays a positive role in these cases.

Special attention should be devoted to the designation of finely ground additives if the use of them is necessary.

The use of high grades of portland cement is required under severe climatic conditions in GOST 4800-59 for hydrotechnical concrete to produce frost resistant concrete, especially for parts of facilities located in a zone with a variable water level. In these cases the use of sulfate resistant portland cement is required in the presence of an aggressive sulfate water medium. For example, grade 400-500 portland cement containing approximately 10% hydraulic additive was used in the facilities of the Volga-Don Construction Project. The cement was sulfate resistant with a limited clinker content of approximately 6% tricalcium aluminate and approximately 50% tricalcium silicate. The use of portland cement with a  $C_3A$  content of not more than 5% and  $C_3S$  at least 45 and not more than 55% in zone A was recommended in accordance with the specifications for cement for the Kuybyshevskiy and Volgogradskiy Hydroconstruction Sites between 1953 and 1955.

The experience of using portland cement with a limited hydraulic additive (opoka or tripoli) and mineralogical clinker content should be carefully studied and considered for other hydrotechnical sites. In any case, it may be firmly stated that use of ordinary pozzuolanic portland cements is not recommended for frost resistant concretes. The permissible amount of active furnace slags in portland cement for frost resistant concretes should be tested in special studies. In this case the question should be decided with consideration of the quality of the slags and cement clinker used.

Repeated tests have demonstrated the low frost resistance of concrete containing slag portland cements, and therefore they must not be used without testing and suitable protection of structures in zones of wetting and freezing of capital facilities. In spite of the previously existent opinion that aggregates of carbonate rock must not be used for hydro-technical concrete, studies have shown the full possibility and feasibility of using them in modern hydrotechnical facilities.

Frost resistance which considerably exceeds the requirements of standards in force may be provided by using a limestone aggregate with approximately 4-5% water absorption when working with first grade portland cement. However, in this case good quality sands must be used. The use of fine or impure argillaceous additives which do not satisfy the requirements of GOST 4800-59 of sands for frost resistant and water impermeable concretes may be allowed only on the basis of the results of special studies.



From the experience of building the Tsimlyanskiy Hydroengineering System and the Volgo-Don Canal, the use of such additives as sulfite-alcohol distillery wash, which are not only plastificators, but also considerably increase the frost resistance of concrete, should be more widely recommended.

The addition of sulfite-alcohol distillery wash in the form of a liquid concentrate in amounts of 0.1-0.2% (dry matter) of the cement mass considerably increases the workability of the concrete mixture and leads to a reduction in the water-cement ratio. Naturally, the question arises of using special factory cements of increased frost resistance at hydro-technical sites. As is well known, 1.5 million m<sup>3</sup> concrete using sulfite-alcohol distillery wash were placed at the Volgo-Don Construction Project. The use of air entraining agents of types SNV and SPD [expansion unknown] is most effective for increasing frost resistance.

Air entraining additives are very widely used in the U.S.A. in building cement-concrete roads.

The vacuum compaction of concrete and water absorbing form-work should be more widely used to impart greater frost resistance and increase the resistance of the concrete surface to abrasion in dam spillway faces, walls, aprons, and so forth.

Measures must be taken to ensure complete consolidation of a concrete mixture when placing it in a facility in order to increase frost resistance as well as in all cases to increase the corrosion resistance of concrete. Density may be increased using an entire complex of measures: correct selection of materials, matching and strict observation of concrete composition, the use of efficient vibrators, addition of special substances, observation of specific requirements in transporting a concrete mixture, vibration vacuum compaction, etc. Portland cements with a reduced content of calcium aluminates and with added sulfite-alcohol distillery wash must be used to form a more durable cement stone structure.

From the experience on the Volga Construction Project, the Volga-Don Construction Project and other hydrotechnical projects, wider use should be made of reinforced concrete shell plates for facing such structures as dams, hydroelectric station buildings, the face surfaces of sluices, etc. Highly mechanized factories should be constructed in good time at large-scale hydrotechnical construction sites to produce flat and molded plates with an area of up to 10 m<sup>2</sup> and thickness 10-30 cm. Aggregates in the form of crushed granite with a coarseness of up to 30 mm as well as sands with good grain composition and 320-360 kg/m<sup>3</sup> grade 400-500 portland cements should be used to make concrete for shell plates. Shell plate concrete should meet requirements for a frost resistance of at least 200-300, water permeability  $W_g$  and rated strength at least 250. If possible a low slump concrete mixture should be used.

To avoid filtration of water through the plate seams, special attention must be devoted to careful vibration consolidation of the concrete adjoining the shell plates, to complete extraction of the wooden racks

edging the plates, and to careful caulking of the seams between the plates with a stiff cement mortar of composition 1:1 (at a W/C = 0.15-0.25). Moreover, to check the quality of the placement it is necessary to make a test boring of the concrete and inject water, and if further consolidation is necessary, to conduct grouting operations on the concrete by injecting cement milk at a pressure of 0.2-0.4 MPa behind the shell plates as a compulsory technological operation in conducting the work.

A study of frost resistance and permeability of concretes subjected to thermal treatment is of interest for factory production of concrete and reinforced concrete structures.

Structural defects which form during early freezing or during thermal treatment (steam curing, electrical heating) greatly affect frost resistance. In this regard a certain analogy may be drawn between early freezing and thermal treatment.

As was already noted, the frost resistance of concretes is provided not only by their high density, but by a specific pore structure as well. For example, cellular concretes with a porosity of 75% and more are more frost resistant after autoclave treatment than dense concretes containing heavy aggregates and a large amount of water. As have been shown by studies and the practice of using normal concretes which harden under various conditions, their frost resistance rises considerably when using air entraining agents, due to which 4-5% closed pores are formed in the cement stone. A reduction in the exposed surface and uniform distribution of pores in the cement stone and concrete considerably raises frost resistance.

The water-cement ratio and harshness of the concrete mixture is of great significance in increasing the frost resistance of heavy and light concretes. At constant and low W/C values, concretes of harsh concrete mixtures have a higher strength and frost resistance.

Samples of workable mixtures containing heavy aggregates at a W/C = 0.6 which were treated in an autoclave were destroyed in tests after 25-50 freezing and thawing cycles, while samples of concretes of similar composition, but with a lower W/C and consisting of more harsh mixtures sustained more than 200 freezing and thawing cycles after the same autoclave treatment.

Mineralogical composition also affects the frost resistance of cements. Increased content of tricalcium aluminate and the addition of crushed mineral agents has a deleterious effect. Analysis shows that when mixing concrete the addition of more than a certain amount of water diversely affects the structure of the construction.

Structural damage to concrete occurs due to the varying direction of the temperature and moisture gradients in thermal treatment, primarily in the contact zone of the aggregate and mortar. This defective structure affects the frost resistance of the material to a greater degree than does the composition of new formations when the cement hardens.

It has been repeatedly noted that concrete frost resistance drops upon steam curing. This is often due to the use of drastic thermal treatment processes and cement composition. However, when using harsh concrete mixtures, well consolidated and with low W/C and added chemical agents, a high degree of concrete frost resistance is attained with moderate thermal treatment.

At ordinary sub-zero temperatures, only the water contained in capillaries with a radius of more than  $0.1 \mu$  causes a volumetric increase; therefore the content of the capillary pores which are formed during cement hydration and sedimentation consolidation of the concrete mixture greatly affects the degree of concrete frost resistance.

It was established by G. I. Gorchakov in his studies that frost resistant concretes should contain not more than 7% capillary pores [13]. In this case it must be considered that the total number of capillary pores drops with time as the cement hydrates and the volume of new formations increases. The lower the water-cement ratio in densely placed concretes, the fewer capillary pores remain in them. In concretes with a low water-cement ratio (less than 0.5) the capillary porosity approaches zero when the cement is completely hydrated. Contraction and gel porosity, on the other hand, increase with time. It is of primary importance to know not the total, but the capillary porosity to estimate the degree of concrete frost resistance.

As is apparent from the results cited below of experiments on steam curing concretes, concrete deformations during heat treatment of them greatly affect frost resistance as well as strength. A study of spontaneous deformations of concretes during steam curing has shown that in all cases steam curing disrupts the concrete structure, sometimes very greatly, sometimes quite insignificantly. Therefore the properties of steam cured concrete are similar to the properties of normally hardened concretes, considering its specific nature. Thus, it is necessary to take into consideration the destructive processes which occur as the result of concrete temperature expansion during heating, in addition to the degree of porosity, type and structure of the pores in it.

Comprehensive studies of concrete frost resistance under severe climatic conditions as a development of the works of S. V. Shestoporov were conducted by G. I. Gorchakov, M. M. Kapkin and O. A. Ptitsyn [13]. They studied concrete resistance as a function of mineralogical composition of cements, the use of surface active agents, size of the water-cement ratio and initial hardening conditions. Concrete of composition of 1:1.5:3.5 (by mass) at a W/C = 0.45 with a 0.5-1 cm mixture slump was studied for frost resistance under laboratory conditions and in the tidal zone of the Kolskiy Bay. Concrete samples  $7 \times 7 \times 7$  cm matched the cross-section of precast reinforced concrete shell plates. Some of the samples were stored under normal conditions, and some were subjected to steam curing under three different conditions: the first - 4 + 12 + 6 hours, the second - 9 + 10 + 3 hours; the third - 8 + 1 + 15 hours at  $80^{\circ}\text{C}$ . All the samples were divided into three groups: the first group was stored the entire time under normal conditions; the second was tested in a freezing



chamber and the samples thawed in natural sea water with a solidity of 35 g/l; the third group was placed on a stand exposed to high and low tides. These samples were completely submerged 5.5-6 hours for the period of a single tidal cycle, and were exposed to the air 6-7 hours.

The results of compression tests of concrete samples in the periods designated by the program are cited in Table 5.17.

Tests have shown that the strength of steam cured concretes containing sulfate resistant cement upon further hardening under normal conditions at ages 28 days and 2 years was higher than the strength of normally hardened concretes. The steam cured concretes were well preserved after 300 alternating freezing and thawing cycles under laboratory conditions; after the 2 year tests under natural conditions steam cured samples containing sulfate resistant portland cement were also rather well-preserved, their strength even increased 15-20% compared to the strength of control samples stored under normal conditions. At the same time the strength of normally hardened concretes increased 7%. After the samples were stored in water for 5 years, their strength increased 50-70% compared to age 28 days. No deterioration of the samples was detected upon examination.

The strength of steam cured samples containing hydrophobic portland cement does not reach the strength of normally hardened concretes at age 28 days and 2 years. Relatively high strength indicators of steam cured concrete containing hydrophobic portland cement from the Volkovysskiy Factory were obtained with steam curing at 80°C under conditions 9 + 10 + 3 hours. After 300 test cycles the strength of the steam cured concretes of the cement increased 30-70% compared to the strength of control samples at age 28 days, and the strength of normally hardened samples only by 20%. It is characteristic that strength of concrete containing hydrophobic portland cement increased during a five-year period of storage in a tidal zone and by the end of this period was 50-80% greater than at age 28 days and somewhat higher than the 2 year strength of normally hardened concrete.

Steam cured concretes containing plasticized portland cement did not attain the strength of concrete of the same age normally hardened upon subsequent normal 2 year storage. Concrete steam cured under conditions 9 + 10 + 3 hours at 80°C had relatively high strength indicators.

The results of frost resistance testing under laboratory and natural conditions show (see Table 5.17) that the second and third steam curing systems with a gradual 8-9 hour temperature rise are more favorable for this plasticized cement. The absolute strength values of steam cured concretes of this cement located on the stand were extremely near the strength indicators of normally hardened concrete. The strength of steam cured concrete containing slag portland cement after 300 cycles of alternate freezing and thawing increased 30-83% compared to the strength of test samples at age 28 days. The strength of normally hardened concretes increased correspondingly 63%.

TABLE 5.17. STRENGTH AND FROST RESISTANCE OF NORMALLY HARDENED AND STEAM CURED CONCRETE

Cement	Preliminary hardening conditions, hours	Compression strength limit without conversion factor, MPa								
		After steam curing	Normally stored under laboratory conditions for		After frost resistance testing under laboratory conditions during cycles of			After storage in the tidal zone for		
			28 days	5 yrs.	100	200	300	6 mos.	2 yrs.	5 yrs.
Grade 400 sulfate resistant portland cement from the Bryanskiy Factory	Normal hardening	—	27,6	35,5	35,6	45,5	38,2	36,2	38	42,7
	Steam cured at 80°C:									
	4+12+6	27,3	28	38,2	33,9	35,4	45,5	35	42,8	47,6
	9+10+3*	18,4	31,7	38,6	41,5	39,6	36,5	35,8	46,2	46,7
	8+1+15	15	30,8	37,9	45,5	41	43	30,2	41,5	—
Grade 300 hydrophobic portland cement from the Volkovysskiy Factory	Normal hardening	—	27,5	39,1	28,6	31,9	33	24,4	32	41,4
	Steam cured at 80°C:									
	4+12+6	11,7	16,2	28,1	27,1	22	27,9	15,5	25,5	29,8
	9+10+3*	14,3	25,7	32,5	29,6	29,6	33,7	22,7	23,3	—
	8+1+15	11,9	19,5	19,5	26,1	29,5	30,1	21,2	21,8	—
Grade 500 plasticized portland cement	Normal hardening	—	43,4	47,4	36,7	40,2	45,6	27,5	37,7	40,7
	Steam cured at 80°C:									
	4+12+6	15,4	22,8	34,3	32,1	32,4	35,7	23,7	50	39
	9+10+3*	24,1	31,7	45,5	44,7	43,9	44,1	25,5	38,3	38,4
	8+1+15	18,5	29,9	32,5	44,4	39,7	41	27,6	31,1	38,6
Grade 300 slag portland cement from the Shurovskiy Factory	Normal hardening	—	25,3	35,8	32,5	39,4	41,3	24,9	38,2	45
	Steam cured at 80°C:									
	4+12+6	14,6	16,6	28,3	25,9	28,8	30,4	20,6	31,7	35,4
	9+10+3*	12,6	20,5	30	27,1	30,3	26,7	17,5	27	31,8
	8+1+15	15,3	21,2	29,7	26,9	33,2	34,4	22,1	32	36

\*Samples gradually cooled in water by reducing the temperature from 80 to 20°C in a 3 hour period.

Commas indicate decimal points.

Five year tests of samples on the stand showed that the strength of concretes containing normally hardened slag portland cement and that of steam cured concretes increased, the concrete steam cured according to the 8 + 1 + 15 hour system at 80°C having the higher strength indicators. Such high indicators of frost resistance of concretes containing various cements after hardening under normal conditions and after steam curing are explained by the use of concretes containing low slump mixes with a W/C = 0.45 which are rather dense and strong. The concrete was steam cured in the forms with a slow temperature rise; this ensured the formation of its structure even at the beginning of the temperature rise and did not result in structural damages.

Thus, analysis of the results of many tests shows that the degree of frost resistance of concrete depends on a number of its characteristics. In this case it must be emphasized that there is no definite dependency between the strength and frost resistance of concrete without consideration of its density and characteristics. As confirmation of this let us cite the results of frost resistance tests of concrete containing 3 cements subject to various types of thermal treatment and then placed in the ground for 18 years and 2 years in a normal storage chamber. As can be seen from Table 5.18, in spite of the rather high strength indicators of concrete at age 22 years (from 16.5 to 46.3 MPa), its frost resistance was low. In concrete subject to thermal treatment, it was moreover lower than in normally hardened concrete. In concretes following thermal treatment (in addition to concrete containing portland cement after ordinary steam curing) the water absorption was greater than in normally hardened concretes. The low frost resistance of these concretes may be due to the fact that workable mixes with a water-cement ratio of 0.67-0.7 were used in making them, then the thermal treatment was carried out before a strong structure had formed. The considerable water saturation of this concrete (from 2.9 to 6.1%) indicates its high degree of capillary porosity. The volume of the pores filled in standard water saturation was 7-14% of the total volume of the concrete. These concretes should also be included among those not resistant to frost according to the theoretical method of evaluating concrete frost resistance proposed by G. I. Gorchakov.

Calculations show that by using quality cements (with a moderate content of the hydraulic component  $C_3A$ ), frost resistant concretes may be obtained only using compositions with a water-cement ratio of no more than 0.5. This water-cement ratio is adopted from the calculation of the filling of the capillary pores with the products of new formations for complete hydration of portland cement, when 25% of the water is bound chemically and 25% by adsorption.

We previously showed that even after concrete remains in a moist atmosphere 18-20 years, the cement stone contains 30-40% non-hydrated clinker particles. Consequently, no more than 60% of the cement participates in hydration. Therefore the theoretical water-cement ratio for concrete with a high degree of frost resistance will be approximately 0.3. In this case the concrete should contain practically no capillary pores which affect its frost resistance. The water contained in the contraction pores and gel pores freezes only at from -30 to -78°C. The presence of this



type of pore not filled with water in the cement stone can have only a favorable effect on the frost resistance of the concrete. In the test examined by us more than half of the mixing water went for the formation of the capillary porosity of the concrete which sharply reduced its frost resistance.

In conjunction with the recent usage of thin-walled reinforced concrete structures of finely graded concretes in construction which are manufactured using the vibration rolling process, the author and V. F. Khvorostyanskiy conducted tests to determine the frost resistance of these concretes.

Samples of mortar with a composition 1:2 and concrete with a composition 1:1:2 were made using portland cements from the Voskresenskiy and Belgorod Factories. Immediately after preparation the samples were steam cured for 3 hours at 100 and 110°C and concomitantly heated in plate form at 100°C. After heating samples at age 1 and 28 days were tested for frost resistance using the standard procedure. Non-heated samples cured under normal conditions for 28 days were tested for frost resistance at the same time. The samples were stored a few days under normal conditions before the frost resistance test.

TABLE 5.18. FROST RESISTANCE OF CONCRETE SUBJECT TO THERMAL TREATMENT AFTER STORAGE IN THE GROUND FOR 18 YEARS AND 2 YEARS UNDER NORMAL CONDITIONS

Cement	Storage conditions before the frost resistance test.	Water saturation, %	Number of freezing-thawing cycles	Mass loss after frost resistance test, %	Strength limit, MPa		Frost resistance factor at the completion of the test
					Before	After	
					Tests for frost resistance		
Portland cement from the Chernor-echenskiy Factory	18 years in the ground, 2 years normal storage	3,4	188	4,5	31,2	12,2	0,39
Pozzuolanic portland cement	The same	4,1	99	9	28,7	6,3	0,22
Slag portland cement	"	4,5	37	6,7	18,9	2,3	0,12
Portland cement from the Chernor-echenskiy Factory	Steam curing at 80°C (2+8+1 hrs.), 18 yrs. in the ground and 2 yrs. under normal conditions	2,9	—	—	46,3	—	—
Pozzuolanic portland cement	The same	5	51	7,1	24	6,2	0,26
Slag portland cement	"	5,5	15	17,5	16,5	4	0,24

Commas indicate decimal points.

In addition to laboratory samples, prisms sawed out of vibration rolled wall panels manufactured at the Lyuberetskiy Factory were tested for frost resistance.

Tests showed that in most cases concretes tested up to 200 cycles under appropriate thermal treatment conditions had a frost resistance factor equal to unity, i.e., the strength of samples thermally treated did not drop and the samples demonstrated the same frost resistance as those normally hardened.

Prisms sawed out of vibration rolled panels manufactured at the Lyuberetskiy Factory sustained more than 100 freezing and thawing cycles and exhibited no apparent damage at a frost resistance factor equal to unity.

Consequently, in spite of the fact that thermal treatment in principle reduces the frost resistance of concrete, and in spite of the possibility of microstructural defects (directed microcracks and pores) appearing in vibration rolled concrete as the result of the drastic heating conditions, its frost resistance was nevertheless rather high. This is due mainly to the fact that as a harsh mixture with a low water-cement ratio (0.28-0.3) and good vibration consolidation, finely graded concrete has a high density and low capillary porosity.

The frost resistance of light concretes containing porous aggregates after thermal treatment is of considerable interest.

According to the data of various researchers, lightweight aggregate concrete of higher grades sustains up to 100-200 and more freezing and thawing cycles. Tests conducted by us have shown that quite frost resistant products may be produced when lightweight aggregate concrete is cured before hygrothermal treatment and before moderate rises and drops in temperature. Observations of lightweight aggregate concrete sample destruction during compression testing shows that samples are destroyed where the mortar is in contact with the coarse aggregate in a case of too harsh thermal treatment conditions. The same phenomenon was observed when testing lightweight aggregate concrete for frost resistance.

Consequently, one cause of the drop of concrete frost resistance upon moist steam treatment is the destruction of the cohesion between the cement stone and coarse aggregate due to temperature-shrinkage deformation; this is observed especially frequently under severe thermal treatment conditions. Therefore thermal treatment without precuring and with a rapid temperature rise leads to a drop in strength and frost resistance of the concrete.

In most light concretes the cement permeates deep into the porous aggregates; this increases their cohesion. Due to the special features of the structure of haydite the relatively dense outer shell of expanded shale aggregate prevents this in lightweight aggregate concrete. The cohesion of normal concretes with dense aggregates is even more so disrupted in thermal treatment.

Lightweight concretes subjected to ordinary steam curing have a relatively lesser frost resistance than after autoclave treatment. Consequently, there is a dependency here different than for concretes containing dense aggregates. Structural disturbances in the contact zone between the coarse aggregate and mortar are observed in a case of thermal treatment of lightweight concretes. At the same time an interaction between the surface of the hydraulically active aggregate and the cement used occurs. It has been established that lightweight aggregate concrete and slag pumice concrete are characterized by greater frost resistance than slag concrete.

In lightweight concretes the effect of the W/C on frost resistance is less pronounced than in normal concretes. This is due to the hygroscopic light aggregates. During manufacture, placement and the first days of hardening some of the water is drawn off by the porous aggregate and does not engender significant defects in the concrete structure. During subsequent hardening the water accumulated by the porous aggregate is absorbed from it by the cement stone and interacts with the cement. These phenomena may explain the considerable increase in frost resistance of cellular concretes with porous aggregates. For example, samples of foam lightweight aggregate concrete sustained 250 freezing cycles, while samples of foam concrete of the same composition, but without the aggregate, sustained only 90 cycles.

The frost resistance of concretes subjected to thermal treatment increases considerably after curing in a moist medium, especially in water.

TABLE 5.19. FROST RESISTANCE OF STEAM CURED CONCRETES WITH COMPLEX ADDITIVES BASED ON ORGANOSILICON COMPOUNDS

Additives		R <sup>com</sup> before beginning the test, MPa	200 cycles		K <sub>fr</sub>	400 cycles		K <sub>fr</sub>
Name	Portion, % of cement mass		R <sup>com</sup> , MPa			R <sup>com</sup> , MPa		
			After test	Control		After test	Control	
Without additive	—	40,5	32,3	42,5	0,76	Destroyed after 225 cycles		
SES + Ca(NO <sub>3</sub> ) <sub>2</sub>	0,1+1,5	42,5	46,5	44,3	1,05	46,5	46,5	1
The same	0,15+1,5	40,9	45	44,1	1,02	43,6	44,5	0,98
SES+NNK(?)	0,1+1,5	41,8	43,8	43,5	1	40,2	43,2	0,93
SASS + Ca(NO <sub>3</sub> ) <sub>2</sub>	0,1+1,5	40	40,7	42	0,97	36,6	42,1	0,87
SASP + Ca(NO <sub>3</sub> ) <sub>2</sub>	0,1+1,5	42	44,5	44,2	1	44,7	45,6	0,98
GKP(?) - 10 + Ca(NO <sub>3</sub> ) <sub>2</sub>	0,1+1,5	41,2	42,6	42,5	1	41,8	43,5	0,96
GKP(?) - 11 + Ca(NO <sub>3</sub> ) <sub>2</sub>	0,1+1,5	40,5	43	43	1	39,9	42,9	0,93

Commas indicate decimal points.



The frost resistance of concrete with complex additives was studied in the corrosion laboratory of the Scientific Research Institute of Concrete and Reinforced Concrete by L. M. Kotova. The tests were conducted in accordance with GOST 4800-59 and using an accelerated procedure when freezing down to  $-60^{\circ}\text{C}$  in an automatic Nem chamber, thawing in fresh water and in artificial sea water with a salinity of 34 g/l. The frost resistance was estimated from the change in concrete strength. Table 5.19 gives data on the results of tests using a standard procedure which make it possible to conclude that the addition of organosilicon compounds together with hardening accelerators considerably increases the frost resistance of steam cured concrete compared to concrete steam cured without additives. In this case complex additives in conjunction with  $\text{SES} + \text{Ca}(\text{NO}_3)_2$  were most effective, the least effective  $\text{SASS} + \text{Ca}(\text{NO}_3)_2$ . Steam cured samples without additives sustained only 225 freezing and thawing cycles, while with all combinations of chemical additives they sustained 400 cycles with a frost resistance factor of at least 0.87. SES is sodium ethyl silicate, and SASS or SASP are water soluble sodium aluminosilicate methyl silicate in the form of a solution or powder respectively.

Studies conducted in the laboratory for accelerating concrete hardening of the Scientific Research Institute of Concrete and Reinforced Concrete discovered a 3-6 fold increase in frost resistance when air entraining agents of types SNV and SPD [expansions unknown] were added.

The accumulated experimental data indicate the feasibility of adding plasticizing agents together with air entraining agents to concretes upon which high requirements for frost resistance are placed. Along with a study of frost resistance after normal hardening or thermal treatment, we studied the frost resistance of concrete frozen at an early age.

The frost resistance of concrete was determined in concrete samples  $10 \times 10 \times 10$  cm of composition 1:2.1:3.7 at a W/C = 0.58 containing Belgorod and Voskresenskiy cements and frozen immediately, and 3, 6, 9, 12, 24 and 72 hours after preparation at  $t = -20^{\circ}\text{C}$  and also immediately after preparation at  $t = -2^{\circ}\text{C}$ . Frost resistance was determined after 28 days of subsequent normal hardening.

Frost resistance was determined according to GOST 10060-62 "Normal Concrete, Method of Determining Frost Resistance". Frost resistance was estimated by the change in the compression strength limit, mass loss and by the frost resistance factor.

A study of frost resistance of concretes frozen at  $-2$  and  $-20^{\circ}\text{C}$  yielded the following results. As a rule, samples frozen immediately after preparation at  $-2^{\circ}\text{C}$  subsequently demonstrated a considerable drop in frost resistance. These studies have shown that sub-zero temperatures near  $0^{\circ}\text{C}$  are most dangerous with regard to early freezing of concrete (Table 5.20).

At these temperatures a structure with a large number of pores with radius from 1 to  $0.1 \mu$  is formed during slow hydration of the cement;

during standard testing of concrete for frost resistance phase transformations of water occur primarily in these pores. Samples frozen at  $-20^{\circ}\text{C}$  and tested for approximately 300 freezing and thawing cycles demonstrated a reduced frost resistance factor compared to the frost resistance of normally hardened samples, but only in tests when they were frozen immediately after preparation. Freezing of samples at the same temperature, after 9 hours of precuring before freezing, and after subsequent normal storage did not reduce frost resistance.

We may conclude that the strength criterion established for evaluating "maturity" at the instant the concrete freezes may be adopted for its density and frost resistance characteristics. Micro- and macrostructural strength and density of concrete are directly dependent and can be used equally to evaluate the durability of concrete during early freezing.

TABLE 5.20. EFFECT OF EARLY FREEZING OF CONCRETE ON ITS FROST RESISTANCE

Curing time before freezing, hours	Freezing temperature, °C	Compression strength, MPa	Frost resistance							
			Compression strength limit, MPa		Compression strength limit, MPa, after cycles of			Frost resistance factor after cycles of		
			Before freezing	At age 28 days	100	200	300	100	200	300
0	—20	22,2	0	22,6	20,1	24,6	25,2	0,68	0,84	0,82
3	—20	20,9	0,16	24,7	24,5	23,1	24,5	0,83	0,79	0,81
6	—20	24,1	0,4	23,2	24,7	27,2	24,2	0,84	0,93	0,79
9	—20	26,9	0,6	26,1	28,5	27,9	30,7	0,97	0,95	1
12	—20	26	0,9	25,7	26	25,5	34,9	0,88	0,87	1
24	—20	28,6	4,3	27,9	28,1	30,9	32,3	0,96	1	1
0	—2	17,8	0	18,3	10,9	11,2	0	0,37	0,38	—
—	Normal hardening 28 days	31,7	—	29,4	26,1	34,8	31,9	0,9	1	1

Commas indicate decimal points.

Note. All samples were cured 3 days in freezing weather and 28 days under normal conditions after thawing.

The question of the effect of various temperatures on water and gas permeability has not been sufficiently treated. At the State All-Union Scientific Research Institute of the Cement Industry M. M. Kapkin conducted comprehensive studies of the effect of steam curing on the water permeability of concrete containing sulfate resistant portland cement with plasticizing and air entraining agents. He concluded that water permeability which satisfies the requirements on hydrotechnical discharge facilities and tunnel casings may be obtained by changing to harsh steam cured concretes. Steam curing with a slow temperature rise to  $80^{\circ}\text{C}$  may be used to increase

the water permeability of concretes under water pressure. The addition of SLW and naphthenate soap to harsh concrete mixtures reduces the water permeability of concrete to be steam cured.

When we considered how little the effect of early freezing on gas and water permeability of concrete has been studied, those of us at the Scientific Research Institute of Concrete and Reinforced Concrete conducted special experiments. Cylindrical samples 10 cm high and 10 cm in diameter of concrete of composition 1:2.1:3.7 with a W/C = 0.58 containing grade 400 Belgorod and Voskresenskiy cements were prepared to study water and gas impermeability. The samples were frozen at  $-20^{\circ}\text{C}$  immediately after preparation and after 3, 6, 9, 12, 24 and 72 hours of precuring under normal conditions, as well as immediately and 24 hours after preparation at  $-2^{\circ}\text{C}$ . The samples were tested 60 days after thawing and subsequent hardening in a normal storage chamber. The samples were tested for gas permeability in a unit made at the experimental factory of the All-Union Scientific Research Institute of Industrial Technology of Precast Reinforced Concrete Structural Parts and Products. The samples were dried at  $60^{\circ}\text{C}$  before testing.

The results of the tests for gas permeability of concrete containing Belgorod cement are shown in Table 5.21, that containing Voskresenskiy portland cement in Figure 5.23.

As can be seen from these data, the freezing of concrete considerably increases its gas permeability. Freezing immediately after preparation increases the gas permeability of concrete 100-200 times.

The precuring of concrete before freezing at an above zero temperature will result in a drop in its gas permeability. In concretes frozen 24 hours after preparation the gas permeability differs little, and in those cured 72 hours before freezing and steam cured with a strength of 13-16 MPa the gas permeability cannot at all be distinguished from the gas permeability of control samples.

Studies of the water permeability of concrete frozen at an early age were conducted according to the procedure of GOST 4800-59 with the singular difference that the water permeability of concrete was monitored according to the greatest pressure on the sample at which the appearance of moist spots on the opposite side of the sample was observed. The effect of freezing of concrete on its water impermeability at a strength near "critical" was studied in concretes with various W/C (0.45 and 0.58) containing different cements.

Tests have shown that freezing of concrete immediately after preparation results in a considerable deterioration in its water permeability, the samples let pass water even at a pressure of 0.1 MPa. Samples frozen 24 hours after preparation (with a strength of 3.5 MPa or 11% of  $R_{28}$ ) differed little with regard to water permeability from samples normally hardened. These samples were water permeable at 0.4 MPa. In all cases concretes frozen after 72 hours subsequently demonstrate the same water



permeability as normally hardened concretes. We may conclude on the basis of these tests that the requirements of SNiP III-V.1-70 with regard to the water permeability of concretes used in winter are extremely high.

TABLE 5.21. EFFECT OF EARLY FREEZING OF CONCRETE CONTAINING BELGOROD PORTLAND CEMENT ON ITS GAS PERMEABILITY

Hardening conditions	Gas permeability, cm <sup>3</sup> /min, at a pressure, MPa						
	0.1	0.2	0.3	0.4	0.5	1	2
Freezing immediately after preparation at -20°C	1270	2100	4200	6600	9800	16 000	—
Frozen 3 hours after preparation at -20°C	720	1720	3930	5600	8400	15 200	32 200
The same after							
6 hrs.	450	1370	2630	4050	6540	12 000	16 400
9 hrs.	205	530	1040	1780	2750	7600	14 200
12 hrs.	100	265	470	740	1100	3400	9800
24 hrs.	35	90	200	270	410	1280	3800
72 hrs.	30	70	120	210	300	1000	3300
23 days of normal hardening	63	125	235	360	550	1080	3300

Note. All samples cured 3 days at -20°C and 60 days after thawing under normal conditions.

The water permeability of concretes under various hardening conditions have also been repeatedly studied in the corrosion laboratory and the laboratory for the acceleration of concrete hardening of the Scientific Research Institute of Concrete and Reinforced Concrete. Tests have shown that both normal and lightweight concretes at small and average W/C values and under moderate thermal treatment conditions do not reduce, but conversely, increase water impermeability. Previously opinions were not quite sound in this regard, and it was considered that thermal treatment must necessarily lead to a reduction in water permeability. The same holds true for frost resistance.

The impression of the negative role of thermal treatment was formulated on the experience that in many cases parts made of concrete and reinforced concrete heated under accelerated conditions were insufficiently frost resistant.

Recent studies have shown that at a low W/C (0.35-0.45) and under mild thermal treatment conditions normal and light concretes are completely frost resistant. They sustain up to 300-400 freezing and thawing cycles.

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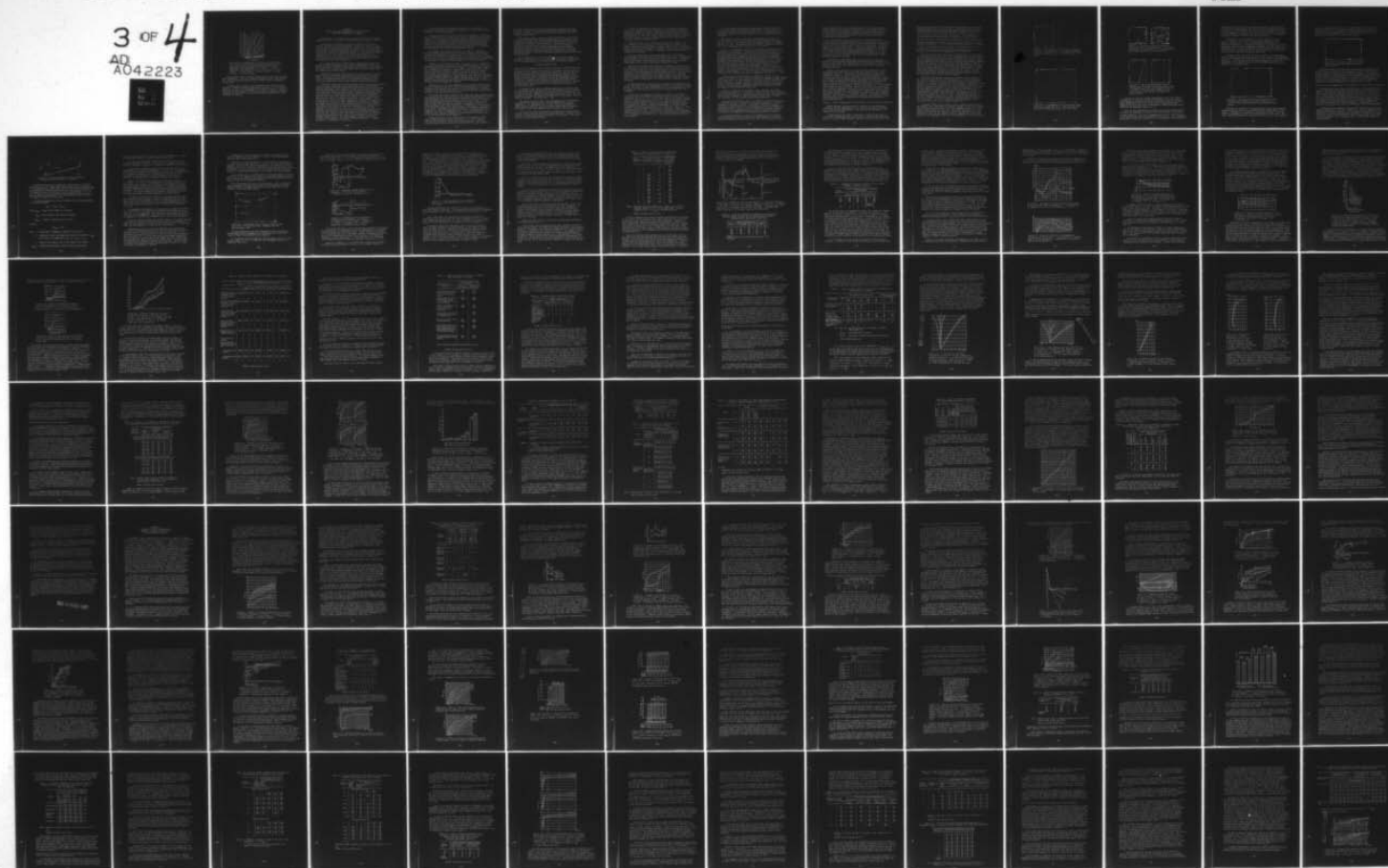
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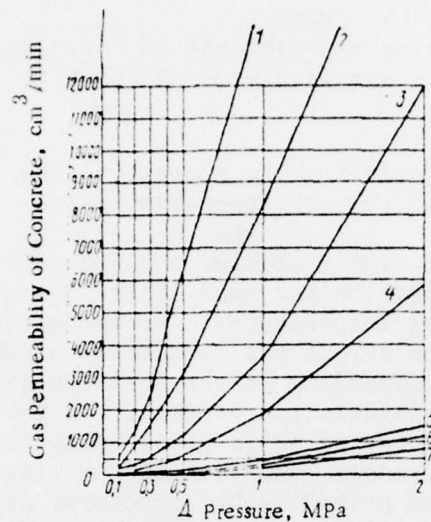


Figure 5.23. Gas Permeability of Concrete of Composition 1:2.1:3.7 With a W/C = 0.58 Containing Voskresenskiy Cement and Crushed Limestone Tested at Age 60 Days and Frozen Immediately After Preparation at  $t = -20^{\circ}\text{C}$ . 1, Frozen immediately after preparation; 2, After 3 hours; 3, After 6 hours; 4, After 9 hours; 5, After 12 hours; 6, After 24 hours; 7, Normal storage.

Sand concretes with a low water-cement ratio are frost resistant and water impermeable. After 200 freezing and thawing cycles, sand concretes with a dense structure withstood testing without a drop in strength in all our tests.

It follows from an analysis of experimental data that the correct selection of cements, concrete compositions (especially W/C) and heating conditions as well as the achievement of the degree of specific "maturity" before the concrete begins to freeze are necessary to impart to concretes impermeability and the previously attained graded strength during thermal treatment and freezing.



CHAPTER 6  
EFFECT OF SUB-ZERO TEMPERATURES ON THE STRUCTURAL  
FORMATION AND HARDENING OF CONCRETE

The formation of the cement stone microstructure during hydrational hardening at above zero and sub-zero temperatures was examined in Chapter 2.

On the basis of experimental studies the author has traced the kinetics and degree of hydration and heat liberation of cement at above zero and sub-zero hardening temperatures. At the early stage of hydration, at the stage of coagulation structural formation, a sub-zero temperature first retards, and later, depending on the duration of its effect, completely disrupts the cement-water interaction process. As the temperature drops further below zero, the amount of solid phase being formed (ice) in hardening cement stone increases, and that of the liquid phase decreases. This process is accompanied primarily by structural changes due to the increasing volume of water becoming ice.

As a strong crystalline structure forms, cement stone acquires the ability to resist the pressure which occurs from expansion. In this case much of the water interacts with the cement clinker minerals and contraction micropores arise. Consequently the cement stone in time no longer undergoes significant structure changes.

Hydration of the cement causes an increase in the volume of the solid phase of the new formations and a decrease in the volume of the liquid phase. The increase in the volume of the contraction pores in the gels causes not expansion deformations, but compression deformations; this favors the preservation of the initial structure which has been formed.

Considerably fewer works have been devoted to the study of macrostructure and the physical changes which occur during the process of temperature action on hardening concrete than have been devoted to studies of the cement stone microstructure. More attention has been given thermal treatment in well known works conducted in recent years on the study of physical changes in the structure of the hardening concrete. Questions associated with imperfections of the cement mortar and concrete when they are frozen at an early age have been little studied or elucidated. Various meanings are attributed the concept of concrete structure by various authors. Some authors reduce it all to the phase composition, dimensions and shape of the crystalline new formations, others consider the distribution, dimensions and number of pores and capillaries permeating the body of the concrete, a third group the uniformity of distribution and density of packing of all components of the concrete [27, 28, 61]. Concrete structure is not invariable, it changes as the result of physical-chemical processes in the hardening concrete as well as by the action of the external medium and loads [13, 49]. Moreover, when some authors discuss structure, they have in mind the hardening concrete, others consider concrete as an already hardened cement material. The latter examine concrete structure in conjunction with the study of its most important properties -- strength, permeability, deformability, durability.

To achieve high physical-mechanical properties in concrete, it is necessary to learn how to control the formation of a dense concrete structure still in its hardening stage.

Studies indicate that the physical-mechanical properties of concrete and its durability with a uniform distribution of components are determined largely by the formation of the physical structure at the hardening stage. Previously it was customary to examine concrete properties in conjunction with the phase composition of the new formations produced during cement hydration. A great deal of attention has been given cement mineralogy and little attention devoted to the structural formation of the concrete on the whole as a macro- and microcompositional material.

For example, the creation of porosity in concrete by adding air entraining agents makes it possible to increase its frost resistance and water and gas impermeability several times in the hardened state. Until recently the role of porous aggregates used in concretes at sub-zero temperatures was poorly studied. Research conducted in recent years has demonstrated the efficiency of using light porous aggregates in winter concreting.

Formation of the concrete structure at the early stage of hardening is associated with volumetric changes in the components caused by the action of the temperature and humidity of the medium. If during normal hardening the structure of the concrete is formed under relatively peaceful conditions, considerable volumetric changes occur during thermal treatment and freezing. Basically these changes occur due to expansion of the mixing water during heating as well as freezing. With regard to entrained air, during thermal treatment it expands together with the water, and during freezing its volume drops. For example, the phenomenon of an internal vacuum is observed when concretes containing porous aggregates are frozen; the system does not expand, but contracts.

Expansion of the individual components of the concrete during freezing as well as heating at the early stage of hardening disrupts the internal structure of the material and leads to residual deformations. Migration of moisture when the steam-air mixture in the pores expands creates internal pressure in the concrete and causes stress.

The studies described in Chapter 2 have shown that after temporary early freezing the degree of cement hydration upon subsequent hardening at an above zero temperature and sufficient humidity conditions differs hardly at all from that hardened under normal conditions for the entire time. Neither does the phase composition of new formations of cement hardened in this manner differ from that normally hardened. Consequently, the drop in concrete strength due to early freezing may be attributed to the disruption of its physical structure, not due to changes in the chemical processes taking place. The indicated expansion of water in concrete results in the separation of cement and aggregate grains, in the disintegration of its structure, thus causing a weakening of the bond between the mortar part of the concrete and the coarse aggregate.

Migration of water to the cooled surface of the aggregate grains leads to the formation of macro-inclusions of ice. This is usually observed under the grains of the coarse dense aggregate. For the ice inclusions which have been formed the moisture from the warmer layers of

the mortar portion moves to the cold layer where it becomes solid and increases in volume. The structures proper are cooled from the surface downward. Patterns and traces from ice formation under the form remain on the structure surface.

When concrete freezes, moisture migrates from the fine capillaries to the ice inclusions which have been formed and which increase in volume. After thawing cavities and caverns remain on the structure surface and throughout the thickness of the concrete; by destroying the solidity of the material they reduce its strength and increase its permeability. Skinning and flaking of the mortar and aggregates are subsequently observed in hardened concretes where ice has accumulated. Accordingly, when concrete freezes structural changes are associated not only with temperature changes, but also with moisture shift-mass transfer which occurs at the same time.

Mass transfer during concrete freezing merits a certain amount of attention. According to A. V. Lykov, the basis principle of matter transfer in a capillary-porous body is expressed by the following formula:

$$J_m = a_n \gamma_0 \Delta U - a_n \delta \Delta T - K_p \Delta P,$$

where factor  $a_n$  characterizes the inertial properties of the body when the potential fields of matter ( $\Delta U$ ) and heat ( $\Delta T$ ) expand. The first term of the equation is an expression of moisture conductivity and indicates that matter is transferred by the moisture gradient of the material. The second term of the equation expresses the hygrothermal conductivity and indicates that moisture is transferred also by the temperature gradient in the body. The third term shows that the transfer of vapor in the capillary body depends on the gradient of overall pressure ( $\Delta P$ ). Moisture is transferred in the direction of lesser temperatures, pressures and moisture content [43].

In conformity with winter concreting conditions, an intensive shift of moisture from warmer internal layers to the periphery occurs initially when the outside air temperature is lower than that in the structure. As the concrete freezes, moisture migrates from the surface inward. Moisture transfer to the cold zone leads to an excess of the liquid phase, until the moment of freezing -- solidification -- ice.

With regard to cement stone, coarse aggregates, metal reinforcement and form-work are characterized by a higher coefficient of thermal conductivity. In conjunction with this ice lenses which weaken the contact between themselves and the hardening cement stone are formed on the surface of the colder components of the concrete and form-work.

In our case we usually mean moisture transfer when we speak of mass transfer. But, along with the shift in water molecules, a transfer of the ions of the dissolved substances contained in it also occurs. Thus, mass transfer is a more general concept.



In order to understand the mechanism of freezing and the hardening processes of concrete at sub-zero temperatures, we prepared samples for studying the hardening of cement, mortar and concrete at the same sub-zero temperatures at the same time we investigated cement hydration. It was established that at  $-2^{\circ}\text{C}$ , for example, concrete samples acquired from 26 to 63% of the strength of samples hardened the same 28 days under normal conditions, and at  $-5^{\circ}\text{C}$  from 6 to 18%.

Concretes frozen at  $-10$ ,  $-20^{\circ}\text{C}$  acquired almost no strength at all. This situation is well confirmed by studies of the heat liberation of cement. When freshly made concrete is cured 10 days at  $-10^{\circ}\text{C}$ , the effect of heat liberation is not detected. Concretes frozen 24 and 72 hours after preparation gain little strength. Consequently, the hydration process is intensified in this case.

After the concrete has reached approximately 70% of its graded strength under normal conditions just as after steam curing, no significant gain in strength is observed in freezing weather below  $-10^{\circ}\text{C}$ . Apparently this should be due to the formation of a dense gelous shell around the cement grains after intense hydration has reached this stage.

The process of hydration by diffusion is hampered by the fact that the free water in the capillaries freezes and the liquid phase loses access to the unreacted particles. Some intensification of cement hydration may occur due to the incorporation of adsorbed water molecules. Upon subsequent hardening at above zero temperatures concretes frozen at an early age demonstrate some acceleration in acquiring strength. The interrupted process of hydration and hardening of cement continues with some acceleration in acquiring strength due to new accumulated gel formations crystallizing out.

It was established in previous works by a number of researchers [19, 22, 35, 49] that at sub-zero temperatures concrete is able to gain strength. However, the theory of concrete hardening at sub-zero temperatures as well as suggestions for practical utilization in construction have not been developed.

On the basis of technological studies, in 1935 I. A. Kireyenko hypothesized that the increase in concrete strength observed by him at a temperature down to  $-8$ ,  $-12^{\circ}\text{C}$  is due to the course of the cement hydration reaction in the solid phase, i.e., with ice. Without conducting thorough physical-chemical studies, especially of the phase transformations of water in freezing weather, he was naturally unable to correctly explain the hardening of concrete at sub-zero temperatures. Some researchers attempted to develop the hypothesis of I. A. Kireyenko. Thus, G. V. Topilskiy notes that the minerals of the cement clinker gain strength at temperatures down to  $-15^{\circ}\text{C}$ . He points out the possibility of solid phase hydration reactions taking place, i.e., the interaction of the cements with ice. He emphasizes the possibility of this kind of interaction in aluminates minerals.

If in fact the hydration reaction took place in the solid phase, the concrete would harden at any sub-zero temperatures. However, this gain of strength in cement and concrete at from 0 to  $-15^{\circ}\text{C}$  is observed with diminishing intensity as the water freezes in the corresponding pores and capillaries.

Many researchers have written about the hardening of concrete in freezing weather. Thus, S. Bergstrom recorded the hardening of concrete down to  $-10^{\circ}\text{C}$ , and A. Nikenen believes that concrete hardens at a temperature down to  $-15^{\circ}\text{C}$ . He suggested that the intensity of concrete hardening below  $0^{\circ}\text{C}$  be considered with a coefficient 0.2-0.4 [83].

Later, I. A. Kireyenko in 1962 [23] set forth a new hypothesis in his monograph on the hardening of cement mortars and concretes at sub-zero temperatures; this hypothesis was based on the work of Van Bemmelen. At sub-zero temperatures the processes of cement hydration are explained by the dehydration of gels during the freezing of the mortar or concrete. He cited curves of the zone of the reversible process of silicic acid gel according to Van Bemmelen who compared the behavior of silicic acid gel both fresh and at age 8 months. In this case attention is drawn to the fact that the fresh gel yields water which will be forced out of the shells of the calcium hydrosilicate being formed. On this basis, I. A. Kireyenko notes that the earlier the concrete is frozen, the greater its strength. He believed the optimum early time for freezing to be 0.5 hours after the cement begins to set. He cites data in this monograph on the intense gain of strength by concrete at temperatures down to  $-22$ , ...  $-25^{\circ}\text{C}$ .

These statements were an attempt to explain the results of tests conducted previously by him in which an increase in strength of cement mortars was obtained after they were frozen at an early age and then hardened under normal conditions. The data obtained by him which was first of interest on the increase in strength of plastic solutions (and later of low-grade concretes containing porous aggregates) after early freezing engendered discussion at the beginning of the thirties.

In 1934, I conducted verifying tests which confirmed the validity of the data published by I. A. Kireyenko. During the tests the conclusion was drawn that precuring of concrete or mortar at low above-zero temperatures before thermal treatment or normal hardening increases their strength. This conclusion in turn caused discussion among specialists.

My report was examined in 1936 at the Congress of the American Society for Materials Testing. On behalf of the society, Professor P. G. Bates conducted an experimental check; it consisted of subjecting concrete containing 3 portland cements to steam curing and autoclave treatment with precuring of up to 7 days at  $2.5^{\circ}\text{C}$ . The results of the check confirmed the validity of the proposed hypothesis concerning the favorable effect of low above-zero temperatures on hardening and strength of concrete.

As we noted previously, a drop in the temperature of the concrete mixture being placed causes retardation of cement hydration, but at the same time increases the solubility of the lime. The less dense shells of

the new formations facilitate the diffusion processes for the water to penetrate deep into the unreacted cement grains. The number of products of new formations increases and the degree of hydration intensifies, including that of the aluminate components of portland cement clinker. At increased hardening temperatures the concrete does not acquire full strength during later periods.

We shall not discuss the mechanism of the formation of a dense concrete structure at temperatures near  $0^{\circ}\text{C}$ . This question is very timely for prefabricated reinforced concrete factories where thermal treatment is used as well as for erecting massive cast in situ structures. It has been treated in several previous works. It should be noted that I suggested prehydration of cement and curing of freshly made concrete at low above-zero temperatures in spite of the proposition published by P. G. Bates at the time in which he recommended prehydration of cement for massive structures by briefly treating it with steam in rotating drums, drying it and then grinding it once more.

On the basis of experimental data obtained, he gave a positive evaluation of the suggestion proposed by the author in a communication on results of the check. This suggestion was also confirmed in works [43, 45] and it has been widely used for 40 years in Soviet as well as foreign building technology.

Studies of the properties of concrete mixtures prepared at various temperatures have shown that as the temperature increases their water requirement increases. Consequently, the consumption of cement must be increased to ensure the same W/C and consistency of the mixtures. It should be noted that in spite of adhering to the requirements with regard to the equality of water-cement ratios, the strength of concrete at age 28 days is less the higher the hardening temperature of the placed mixture. This is explained not only by the somewhat differing type of shell structure of the new formations at various temperatures, but by the increased water content per unit of volume. The density of cement stone (concrete) at an increased temperature is less since in this case more water is added than at lower temperatures. Therefore if more cement must be used during hot weather compared to a normal temperature, under winter and spring-fall conditions some saving of it is possible. However, when concrete hardens favorable conditions for its gaining strength must be ensured in all cases. These suggestions should be reflected in standardization documents for concreting operations.

#### Effect of Sub-Zero Temperatures on the Formation of the Structure of Concrete.

Before turning to an examination of test data on the hardening of concrete at sub-zero temperatures, let us look at the results of studies of the effect of freezing weather on the structure and deformability of concrete at an early age.

In molecular physics water is regarded as a system of molecules in oscillatory, translational and rotary motions. When the water temperature drops the internal energy decreases, auto-diffusion of the molecules slows



down, and the probability of the occurrence and growth of crystallization centers arranged in the form of an open ice structure increases. The temperature affects the binding and separation of some of the most simple water molecules. Thus, for example, molecules composed of  $H_2O$  exist only in vaporous water at very high temperatures. At temperatures of 100-200°C the water vapor molecules are composed of  $(H_2O)_2$ -dihydrol. Near 100°C molecules of liquid water are composed of  $(H_2O)_3$ -trihydrol, and at lower temperatures the number of them gradually diminishes due to the doubling of trihydrols, i.e., the formation of  $(H_2O)_6$  molecules. Molecules of  $(H_2O)_{12}$  are produced in the solid phase. The activity of water in chemical reactions diminishes significantly at critical points, i.e., at 0 and 100°C, as the result of the aggregation of its molecules.

When water freezes its volume increases approximately 9% (the density of ice when pure water freezes is 0.917, and higher for mineralized water). Swelling and shearing of grains caused by freezing of the concrete mixture or a low-strength placed concrete in the contacts of its components leads to the disruption of the cohesion between individual grains of the materials composing the concrete not yet sufficiently cemented among one another. The very fine ice layers which form disrupt the contact between the cement mortar and coarse aggregate as well as the metal reinforcement. Repeated freezing and thawing of concrete, as takes place in late fall and early spring when volumetric expansion and contraction of it occur, disrupt even more the internal cohesion between the component materials and lead to an increase in the loss of concrete strength.

The surface and internal structure of concrete is not disrupted in the same way at different sub-zero temperatures. At a lower temperature more fine ice crystals are formed, and after thawing a great number of fine pores is observed in the structure of the concrete. When water freezes rapidly it is not able to migrate to the cooling front. Therefore it does not accumulate and freeze on the surface of the concrete in the form of large needles and lenses. Figure 6.1 shows the structure of the outside surface of samples after they are frozen at  $t = -5$  and  $-50^\circ C$  and then hardened at an above-zero temperature. Approximately the same structure is obtained at  $-2^\circ C$  as at  $-5^\circ C$ . Tests show that freezing at sub-zero temperatures near zero is usually reflected more graphically in the drop in strength and frost resistance of concrete than at lower sub-zero temperatures. At  $-20^\circ C$  considerable structural damage is still observed on the surface of test samples (Figure 6.2).

Structural damage to the concrete itself is usually characterized by the formation of a large number of capillary channels in the mortar portion and cavities under the grains of the coarse aggregate (Figure 6.3). This picture becomes especially clear when using gravel from hard rock. When using porous limestone and especially light porous aggregates, cavities and frost patterns are not observed under the fragments of crushed stone. Therefore porous aggregates should be shown preference in winter concreting.

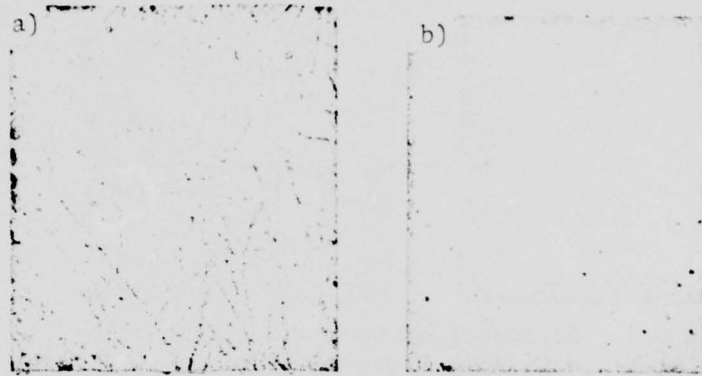


Figure 6.1. Imperfections on the Surface of Samples in Contact With a Metal Form. The samples were frozen soon after preparation: a, at  $t = -5^{\circ}\text{C}$ ; b, at  $t = -50^{\circ}\text{C}$ .



Figure 6.2. Microphotograph of the Surface of Cement Stone Frozen Immediately at  $t = -20^{\circ}\text{C}$  and Cured 28 Days After Thawing Under Normal Conditions (X10).



Figure 6.3. Structure of Concrete (Composition 1:2:4 at W/C = 0.7) in Cross-Section. a, Concrete frozen soon after preparation; b, Concrete hardened under normal conditions for the entire time.

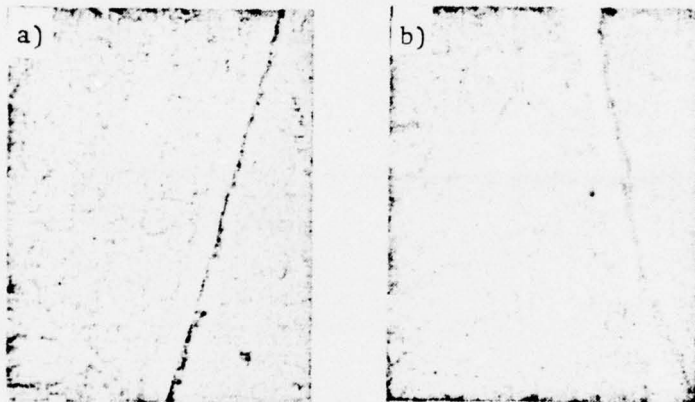


Figure 6.4. Zone of Contact Between a Quartz Aggregate and the Cement Stone Following the Action of a Temperature of  $-5^{\circ}\text{C}$  and Subsequent Hardening. a, 3 days; b, The same, after hardening under normal conditions for 180 days (polished micro-sections X125).

Cavities in the zone of water accumulation on the cold surface of the aggregate are formed in concrete, for example, containing a dense quartz aggregate after freezing in the freshly made state and subsequent normal hardening (Figure 6.4). At age 3 days of subsequent normal hardening the cavity was fixed in the form of a border around the entire surface of the aggregate (Figure 6.4, a).

After 180 days hardening under normal conditions the cavity between the mortar and aggregate was filled by crystals of  $\text{Ca}(\text{OH})_2$  as the result of cement hydration. So-called "autogenous healing" and solidification of the internal structure of the concrete have occurred. These interesting microscopic studies were conducted by S. Kh. Yarlushkina at the Scientific



Research Institute of Concrete and Reinforced Concrete; she studied the cohesion between the aggregate and mortar at various temperatures affecting the concrete. A different picture is observed after concrete containing limestone aggregate is frozen. These cavities are not formed in the zone of contact between the aggregate and the mortar (Figure 6.5), although an insignificant border is visible under the microscope.

Considerable structural damage may occur in the mortar as well as in the concrete. The extent of these damages depends on water content, placement density, rate and temperature of freezing. As is apparent from Figure 6.6, cement mortar containing light porous aggregates may undergo clear structural damage upon freezing. We took a sample of this mortar when erecting the Ministry of Light Industry building in Moscow on Kirov Street. In erecting walls of large blocks of artiksk [arctic?] tuff sand of the same tuff was used in the mortar.

In concrete almost 75% of the volume is occupied by the aggregates. Therefore the quality, dimensions and state of the surface of the aggregates play a very important role in producing concretes of set building-engineering properties. As the dimensions of the coarse aggregates increase, the concentration of stresses in the body of the concrete grows and the homogeneity of its structure drops.



Figure 6.5. Microsection of Concrete Containing Crushed Limestone (X100) Frozen 3 Hours After Preparation at  $t = -20^{\circ}\text{C}$  and cured 28 days under normal conditions after thawing.

Properties of thixotropy of concrete mixtures appear when using fine aggregates and the structure is characterized by a large degree of homogeneity. Deformability is greater in fine graded concretes. The more coarse the aggregates, the more the concrete tends to form cracks. However, a more rigid skeleton is formed in this case; this is very important

in order to reduce the deformability of loaded concrete. During winter concreting the role of the aggregates acquires even greater significance. Therefore we believe it necessary to call the attention of builders to the selection of the aggregates and the consideration of their specific properties when concrete is frozen at various ages.

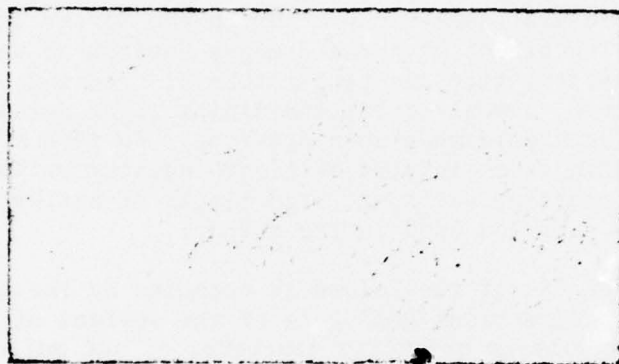


Figure 6.6. Structural Imperfection of Cement Mortar Containing Light Aggregate Caused by Early Freezing.

Volumetric changes in concrete upon freezing reduce the density and are reflected in the cohesion of the aggregate and the cement stone; this reduces bending strength more than compression strength. The danger of concrete damage is reduced when using porous aggregates with great deformability compared to dense aggregates. Besides those parameters which are recorded in the theoretical formula, the strength of concrete depends on the quality of the aggregates and their cohesion with the cement mortar. Studies of micro- and macrostructure of concrete emphasize this.

#### Effect of Sub-Zero Temperatures on the Deformability and Porosity of Concrete.

We studied structural changes in cement paste, mortar and concrete by measuring expansion and contraction during freezing and thawing soon after samples in the form of prisms were prepared from them. The modulus of elasticity was studied in hardened concrete after freezing it at an early age. A great deal of experimental material, part of which is cited below, has been accumulated in the laboratory during the past 15 years. First we developed a procedure and built a device to determine concrete deformation during the process of freezing the prisms in cooling chambers as well as during thawing and subsequent hardening. Temperatures of  $-5$ ,  $-10$  and  $-20^{\circ}\text{C}$ , in special cases  $-50^{\circ}\text{C}$ , were maintained in the cooling chambers.

Deformations were measured using clock-type indicators with  $0.01\text{ mm}$  graduation mounted on a steel base (Figure 6.7). Then the cement stone and concrete were tested for porosity, water absorption and permeability. In doing this the strength characteristics and moduli of elasticity of normal and light concretes frozen immediately after preparation and at age 1 and 3 days were studied. Ye. G. Glazyrina and L. A. Belova participated in the experiments.



Figure 6.7. Device for Measuring Linear Deformations of Concrete and Mortar Prisms 7 x 7 x 28 cm.

Measuring devices and all rubbing and rotating parts of them were lubricated with an antifreeze grease when working in the cold chambers. To study deformations, copper pipes 2 mm thick with feelers welded to them which enhanced the cohesion of the plate with the concrete in which it was embedded were set into the ends of small concrete beams 7 x 7 x 28 cm. With this system for measuring linear deformations the indicator readings depend on deformations of the sample being tested as well as on the change in length of the steel base.

The following formula was used to determine true linear deformations of the concrete sample

$$\Delta E_{\text{sam}} = \Delta E_{\text{ind}} - \Delta E_{\text{base}},$$

where  $\Delta E_{\text{sam}}$  - change in the length of the sample;

$\Delta E_{\text{ind}}$  - total change in the indicator readings;

$\Delta E_{\text{base}}$  - change in length of the steel base.

In turn:

$$\Delta E_{\text{base}} = \alpha \Delta t l,$$

where  $\alpha$  - coefficient of temperature expansion of the steel;

$\Delta t$  - difference between the temperature during the experiment ( $t_{\text{exp}}$ ) and initial test temperature ( $t_{\text{ini}}$ )  $\Delta t = t_{\text{exp}} - t_{\text{ini}}$ ;

$l$  - length of the support equal to the length of the sample;

$\Delta E_{\text{base}}$  - determined experimentally when the base was operating;



to do this a quartz tube, the length of which corresponded to the length of the concrete sample, was placed between the indicators.

The curves are subsequently plotted from the total changes in the indicator reading as a function of the time of the change in length of the steel base and a second curve is graphically subtracted from the first.

Calibration was conducted to determine the correctness of the indicator readings at a sub-zero temperature. To do this the deformations of the base were experimentally determined at various sub-zero temperatures. The experimental points lay on a straight-line, the slope of which characterizes the coefficient of linear expansion of the steel. In actuality the deformations were measured in the following manner.

Samples with metal plates embedded in the ends were prepared in metal forms  $7 \times 7 \times 28$  cm. After preparation the sample remained in the form 20-40 minutes depending on consistency, and the edges of the form were removed and the sample left on the pallet. At this point the beam and pallet together were placed in the device, the indicators screwed on underneath, the head touching the plates and the indicators fixed with a set screw. The initial reading of the indicators was assumed to be zero. The device and sample were placed together in a cooling chamber.

Subsequently readings were taken every 5-10 minutes for the first 3 hours, and then every 30 minutes. After 4-5 clock measurements a sample was left in the cooling chamber until the next morning, then left out under normal or dry air conditions. Upon thawing measurements were taken every 15-20 minutes, and every hour (for the first days), subsequently once a day.

The contraction deformations of the cement paste, mortar and concrete were studied first of all under normal conditions at the same W/C at an early age. It was established that cement paste, then mortar and concrete, yield the largest contraction. Later the effect of the type and amount of aggregates on the amount of deformation at an early age was determined.

Tests show that the greater the strength (density) of a coarse aggregate in concrete, the greater its contraction at an early age, although the amount of cement glue and the W/C were the same in all cases. At the same time, the more aggregate by volume, the less contraction.

Deformations caused by a sub-zero temperature were studied first in a paste of normal thickness, and also with a W/C equal to the W/C of concrete cured for different periods of time before freezing. It was established that cement paste with a W/C equal to the W/C of the concrete which was assumed to 0.4 in the tests exhibits the greatest deformations and the appearance of cracks when frozen immediately after preparation. The experiment has clearly shown that the cement stone is the basic cause of contraction and volumetric deformations in concrete. Only the curing of concrete for 20 hours eliminates the appearance of cracks in it when the amount of deformation is reduced.

Deformations of mortar samples were studied at the same W/C and cement consumptions as in the concrete. In this case the deformations were less than in the cement paste.

Addition of a coarse aggregate to the mortar reduces deformations even more when the samples are frozen, concrete with light water saturated aggregates exhibiting the greatest deformations, and concrete with heavy aggregates the least. This was established by measuring deformation during the process of freezing concretes with an identical amount of water and quantity of cement mortar containing an equal amount of coarse aggregate.

If we consider that the harmful effect of freezing weather on concrete lies mainly in the change in its structure in the initial formation period, let us examine the results of the studies of concrete deformations during freezing, thawing and subsequent hardening.

The following materials were used in the tests: grade 400 Belgorod cement and grade 500 Novorossiyskiy cement (GOST 10178-62),  $1400 \text{ kg/m}^3$  crushed limestone with grain sizes from 5 to 15 mm (GOST 8267-56) and  $1500 \text{ kg/m}^3$  river sand (GOST 8736-62).



Figure 6.8. Imperfections Due to Freezing a Cement Paste With a W/C = 0.4 at an Early Age. Temperature of the cooling chamber  $-20^{\circ}\text{C}$ .

Freezing deformations were first measured in normal concretes of varying compositions at temperatures of the medium of  $-10$  and  $-20^{\circ}\text{C}$ . Figure 6.9 shows the deformation curve obtained.

It is apparent from the graph that when the sample was first in the cooling chamber ( $\approx 1$  hour) it contracts, then elongates, finally its dimensions stabilized.

Contraction during freezing depends on the rate of cooling; as the temperature drops from zero it diminishes and proceeds more rapidly. Thus, for example, when  $t = -10^{\circ}\text{C}$  the contraction continues for 4.5 hours and is 1.575 mm/m, and at  $-20^{\circ}\text{C}$  it is 1 hour and 0.875 mm/m (Figure 6.10).

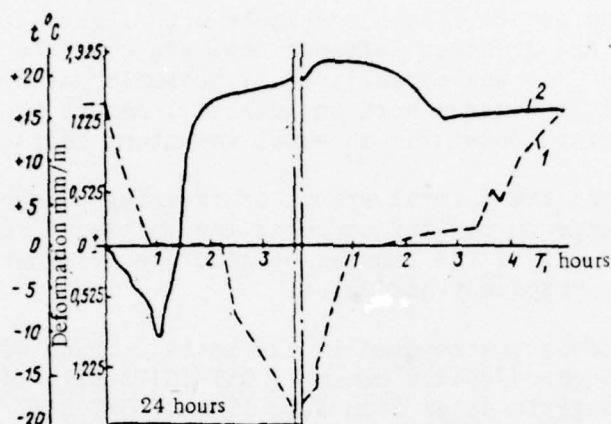


Figure 6.9. Dependency Between Deformations and Temperature in the Center of the Sample.

1, Temperature curve; 2, Deformation curve.

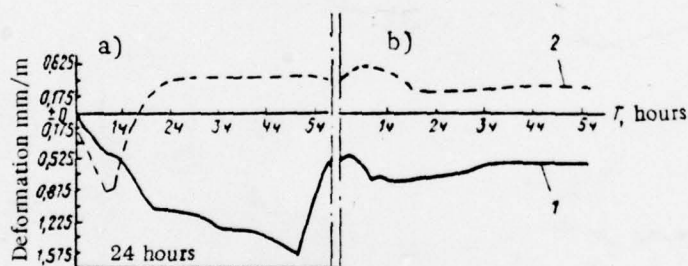


Figure 6.10. Deformations During Freezing and Thawing of Concrete Samples. a, Freezing; b, Thawing at  $t = 15^{\circ}\text{C}$ ,  $W = 95\%$ ; 1, Freezing at  $t = -10^{\circ}\text{C}$ ; 2, The same,  $-20^{\circ}\text{C}$ . (Concrete composition 1:2.25:3.75 at a  $W/C = 0.5$ ).

The initial reduction in size of the prisms is caused by the increase in water density, the compression of the solid components as the temperatures drop as well as by moisture losses. Before becoming ice the water is in an unbound state due to the drop in the rate of cement hydration at the sub-zero temperatures; therefore the intensity of its evaporation increases. This is accompanied by a sharp reduction in the dimensions of the sample, especially during slow cooling (4.5 hours at  $t = -10^{\circ}\text{C}$ ).

Expansion (elongation) of the freshly made concrete upon freezing is the result of water becoming ice, since its low strength coagulation



structure is not able to resist the pressure of the expanding water (Figure 6.11). This expansion occurs primarily as the temperature passes through  $0^{\circ}\text{C}$ , since a sharp decrease in the rate of hydration at the sub-zero temperatures determines the presence of free, chemically unbound water. The temperature curve in the center of the sample which was recorded at the same time together with the deformation measurements indicates this fact (see Figure 6.9). When the concrete was thawed 30-40 minutes some increase in its dimensions is noted (approximately  $0.175 \text{ mm/m}$ ); in doing this the temperature of the sample rises. At the instant the ice melts, contraction occurs which is associated with self-consolidation of the concrete due to the reduction in volume of the thawed water. Subsequently, the concrete again expands insignificantly. This process may continue 2-3 days, alternating then with ordinary moisture contractions.

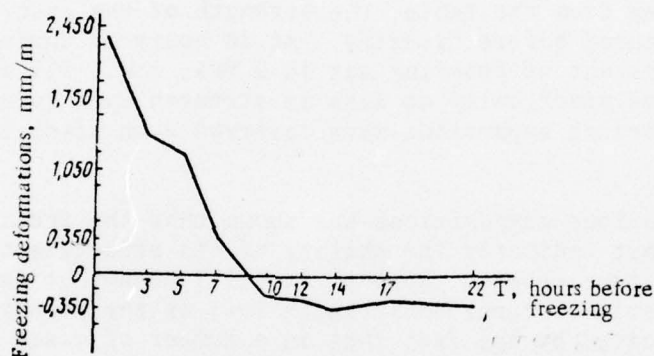


Figure 6.11. Freezing Expansion as a Function of Precuring (Concrete Composition 1:2.1:3.7 at a  $\text{W/C} = 0.65$ ).

Freezing deformations as a function of  $\text{W/C}$  with a fixed amount of water were checked in the work. It was established that as the  $\text{W/C}$  increases freezing expansion rises, being most intense in the  $\text{W/C}$  range of 0.33 to 0.5.

On the other hand, the contraction which proceeds the expansion diminishes as the  $\text{W/C}$  increases, reaching the maximum at a  $\text{W/C} = 0.33$  and with a cement consumption of 600 kg. Thus, contraction to a large extent depends on cement consumption, and elongation on water consumption.

Precuring at above-zero temperatures exerts the most considerable effect on sample deformations during freezing. As the length of curing before freezing increases, contractions and expansions drop and finally, almost no expansion at all is observed in concrete 10 hours old. It alternates with the decrease in the dimensions. When the curing time is increased before freezing, thawing expansion increases and reaches a maximum  $0.7 \text{ mm/m}$  at 22 hours curing. In this case the nature of the expansion changes as well: beginning with 10 hours of curing it exhibits an even character and alternates with contraction only after 24 hours.

The absence of expansion at 10 hours of curing is associated with the fact that during this period chemical and adsorption binding of the water by developing new formations occurs and subsequent consolidation of the hardening system by the crystals of calcium aluminates and aluminoferrites also proceeds.

Concomitant with measurements of deformations of prisms cured before freezing, cubes  $10 \times 10 \times 10$  cm stored under the same conditions as the prisms being tested were made. The composition of the concrete was 1:2.1:3.73 at a W/C = 0.65,  $R_{28} = 33$  MPa, slump 2 cm. Their cubic strength was determined at age 28 days of normal hardening after freezing. Table 6.1 shows the results of these tests.

As can be seen from the table, the strength of the concrete increases the longer it is cured before freezing. At 48 hours of curing, when the strength at the instant of freezing was 10.2 MPa, i.e., 31% of the rated strength, there was practically no loss in strength upon subsequent 28 day hardening. No freezing expansions were observed even after 10 hours of curing.

A study of various compositions has shown that the freezing expansion of concrete at least indicates the ability of its structure to change when exposed to temperature effects, however it still cannot be used as a direct characteristic of concrete strength loss as the result of freezing. This is also indicated by the fact that in a number of cases there is no loss of strength by concrete when the freezing expansion is great, while it is considerable when the expansion is negligible.

Similar data were also obtained by Arvo Nikenen [83]. In his tests the greatest expansion upon freezing immediately after preparation was noted in concrete with a W/C = 0.8 with the same water consumption, however upon subsequent 28 day storage it acquired 101% of the rated strength. This again confirms the lack of a direct dependency between freezing expansion and strength losses. In our work concretes and mortars of plastic consistency repeatedly acquired a strength above the rated after freezing.

Figure 6.12 shows a curve of the course of deformations developed by correlating numerous tests.

It can be seen from the graph that the sample contracts when first in the cooling chamber, then begins to enlarge, and finally, the dimensions stabilize. It shortens quite negligibly (approximately 0.035 mm/m) after reaching the maximum size and actual stabilization. The length of time in the cooling chamber does not substantially affect sample deformations, although a hardly noticeable decrease in size (approximately 0.0175 mm/m) is observed. We may conclude that freezing expansion characterizes the intensity of the effect of the sub-zero temperature on the concrete as well as the inability of the weak structure to resist the pressure of freezing water.

TABLE 6.1. EFFECT OF PRECURING ON THE STRENGTH AND DEFORMATION OF CONCRETE FROZEN AT AN EARLY AGE

Length of precuring before freezing, hrs.	Initial strength of concrete before freezing	Expansion deformations during freezing, mm/m	Sample strength after 28 days of normal storage following 24 hrs. of freezing
0	—	2,275	$\frac{23.1}{70}$
3	—	1,4	$\frac{23.6}{71}$
5	$\frac{0.1}{0.33}$	1,225	$\frac{23.8}{72}$
7	$\frac{0.3}{0.99}$	0,35	$\frac{24.6}{75}$
10	$\frac{0.5}{1.5}$	-0,26	$\frac{23.8}{72}$
12	$\frac{0.66}{2}$	-0,262	$\frac{24.1}{73}$
14	$\frac{0.825}{2.5}$	-0,35	$\frac{27.2}{82}$
17	$\frac{1.32}{4}$	-0,265	$\frac{27.1}{82}$
22	$\frac{3.3}{10}$	-0,305	$\frac{29.4}{89}$
48	$\frac{10.2}{31}$	-0,087	$\frac{31.2}{95}$

Notes. Numerator indicates compression strength limit in MPa of concrete samples 10 x 10 x 10 cm; denominator indicates strength limit in % of  $R_{28}$  of unfrozen concrete.

Commas indicate decimal points.

Residual expansion after thawing indicates deconsolidation and damage to the solidity of the concrete; this creates conditions for irreversible structural changes later on at an above-zero temperature. However, no direct proportional dependency between concrete expansion during freezing and strength losses by it upon subsequent hardening at above-zero temperatures has been established. This is explained by the fact that a short precuring time (10-12 hours) leads to cement hydration and some strengthening caused primarily by the hardening of the aluminate minerals developing in crystalline form.

Thus, the structure formed during curing is already able to take up the pressure of the freezing water which was left over without expansion. However, in spite of this the concrete nevertheless does not acquire full strength later on during hardening at above-zero temperatures. Apparently this is due to the dislocation of the developing structure of the new formations of silicate minerals (gel) which is subsequently not completely restored. With a longer curing time a considerable increase in strength,



approximately 30-40% of  $R_{28}$ , occurs which is due to the aluminate and silicate minerals already beginning to harden. By this time the macro- and microstructure have already basically been formed and the action of freezing weather does not engender imperfections in the concrete which are able to affect its strength.

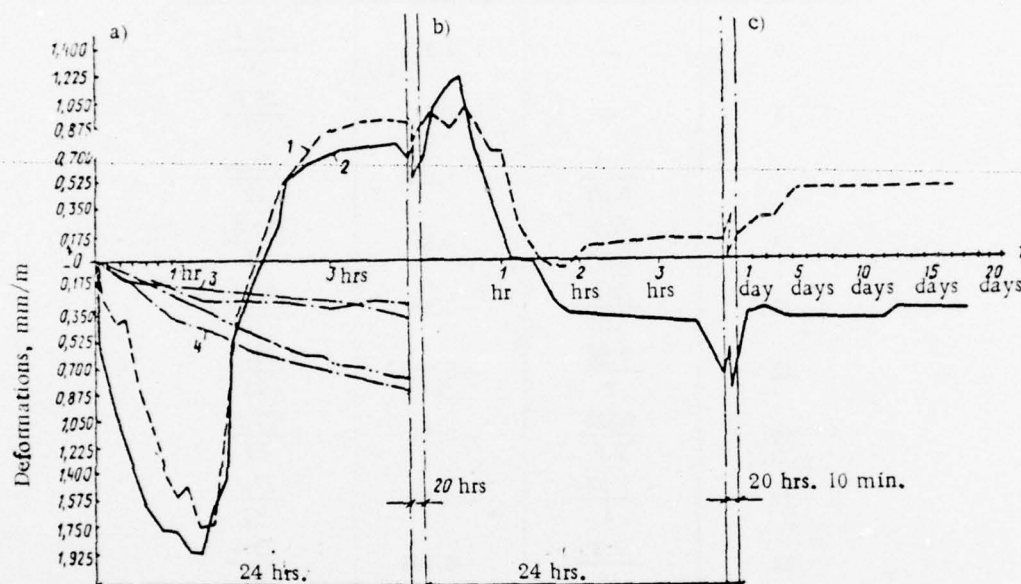


Figure 6.12. Deformations of a Concrete Sample 7 x 7 x 28 cm of Composition 1:2.25:3.75 at a W/C = 0.5 Under Various Temperature Conditions. a, Freezing at  $t = -18^{\circ}\text{C}$ ; b, Thawing; c, Subsequent storage; 1, Thawing under normal conditions; 2, The same, under dry air conditions; 3, Storage under normal conditions; 4, The same, under dry air conditions.

TABLE 6.2. EFFECT OF TEMPERATURE ON DEFORMATIONS OF AGLOPORITE CONCRETE DURING FREEZING AND ITS STRENGTH UPON SUBSEQUENT STORAGE 28 DAYS UNDER NORMAL CONDITIONS

Freezing temperature, $^{\circ}\text{C}$	Maximum deformation during freez. concrete of grade		Strength of concrete*of grade	
	150	400	150	400
-3	461	20	98	71
-10	260	219	93	—
-15	174	149	91	83
-20	142	90	90	85
-30	65	62	86	86

\*Strength of concrete at age 28 days after 72 hours freezing at  $-20^{\circ}\text{C}$  in % of  $R_{28}$ .

Deformations of light concrete during freezing have been studied on the same beam samples covered on four sides (on each side) with a polyethylene coating. The formed samples were stripped as soon as the form could be removed; afterwards they were placed on a pallet with indicators attached to it in the cooling chamber. Deformations were measured during the freezing process at  $t = -3, -10, -15, -20, -30^{\circ}\text{C}$  and thawing on samples containing grades 150 and 400 agloporite concrete. These deformations were compared to deformations of concrete containing crushed granite. The measurement results are shown in Tables 6.2 and 6.3.

It can be seen from these data that as the temperature drops deformations of grade 150 light concrete diminish. They are at maximum, 461, at  $-3^{\circ}\text{C}$ , at minimum, 71, at  $-30^{\circ}\text{C}$ . The process of ice formation is retarded as freezing proceeds more slowly. At a low sub-zero temperature the process of ice formation begins earlier, shrinkage (reduction in size before freezing) is greater, and freezing expansion is less. Thus, when grade 150 agloporite concrete freezes slowly, strong deconsolidation of the concrete occurs as the result of the crystallization pressure of ice.

TABLE 6.3. DEPENDENCY OF FREEZING DEFORMATION ON THE TYPE OF AGGREGATE (IN RELATIVE UNITS)

Freezing temperature, $^{\circ}\text{C}$	Maximum deformation during the freezing process of concrete of grade			
	150		400	
	Agloporite	Granite	Agloporite	Granite
-3	461	255	20	-84
-10	260	275	219	260
-15	174	230	149	182
-20	142	185	90	165
			With the same workability	
-30	65	73	62	92

During freezing at all temperatures except  $-30^{\circ}\text{C}$ , grade 400 concrete exhibits somewhat fewer deformations. The principal difference in the behavior of concrete is observed at  $-3^{\circ}\text{C}$  ( $-5^{\circ}\text{C}$ ). If grade 150 concrete demonstrates maximum expansion as the result of freezing at  $-3^{\circ}\text{C}$ , grade 400 concrete demonstrates minimum expansion. Grade 400 concrete contracts for approximately 3 hours and reaches a maximum value, 135, then ice slowly begins to be formed which lasts approximately 6.5 hours. On the whole, grade 400 concrete freezes more slowly than grade 150 concrete. Since the contraction was significant, the expansion which takes place very slowly hardly increases the initial size of the sample, and in some cases does not increase it at all. During a period of slow cooling the sample is under low above-zero temperature conditions for some time. In this case the processes of dissolution and saturation of the liquid phase by products of cement hydration and the binding of free water by electro-molecular forces of attraction by the surface of the solid particles occurs.

At  $-7^{\circ}\text{C}$  (Figure 6.13) the contraction caused by binding of water diminishes, the process of ice formation begins earlier and proceeds more

intensely both in terms of time as well as magnitude; vigorous expansion of the system is observed in conjunction with this. But if grade 150 concrete does not disrupt any of the forming structure by its maximum expansion, since that structure does not exist, when grade 400 concrete expands the incipient bonds are nonetheless disrupted, although insignificantly, and internal stresses appear. At  $-30^{\circ}\text{C}$  the deformations of concretes of both grades are approximately equal, the freezing rate is high, the process of ice formation occurs rapidly, ice is not able to collect and intense expansion is not observed.

Deformations of concretes containing agloporite and crushed granite were compared at the same temperatures (see Table 6.3). It was established that at the sub-zero temperature deformations of concrete containing crushed granite with the same initial water content and same grade of concrete were somewhat greater than for agloporite concrete. This is due to the fact that a lightweight aggregate draws off part of the water, thus reducing the total amount of water in the mortar portion and the actual W/C. The result of measuring deformation of concretes with a W/C = 0.4 and 155 m of water containing 700 l of dry and wet agloporite is shown in Figure 6.14.

It can be seen from the drawing that concrete containing wet agloporite contracts and expands more than that containing dry agloporite. In concrete containing dry agloporite the great strength under normal conditions, 36 MPa for dry and 26 MPa for wet, indicates a reduction in the actual water-cement ratio.

The results of the change in strength of these concretes frozen at  $t = -20^{\circ}\text{C}$  and then hardened 28 days in a normal storage chamber show that there were no losses of strength in either case as the result of freezing. The strength of concrete containing dry agloporite is 38 MPa, i.e., 106% of the control sample, and that of wet 26.5 MPa, i.e., 102%. Once more this indicates that there is no direct dependence between the loss of strength and residual deformations after freezing and the presence of the latter is not always accompanied by strength losses after thawing.

At  $t = -3^{\circ}\text{C}$  one exception is noted in the behavior of normal and light concrete during freezing. At this temperature, deformations of concrete containing agloporite were greater than of that containing granite.

In cooling down to  $0^{\circ}\text{C}$ , concrete containing crushed granite at this same temperature shows greater contraction, and the expansion which then occurs is less than in light concrete. This is due to the fact that agloporite has a macroporous structure, as the result of which almost all the water drawn in by it from the cement solution is cast into coarse crystals when it becomes ice. At sub-zero temperatures near  $0^{\circ}\text{C}$  these crystals enlarge even more by drawing water from the mortar portion adjacent to the grains. Thus, the optimum conditions for microscopic segregation of ice are created in agloporite concrete; this leads to an increase in deformation compared to concrete containing granite.

However, the further below zero the temperature, the higher the rate of freezing and the less the difference in deformations between concrete



grades becomes. Thus, for example, at  $t = -30^{\circ}\text{C}$  deformations of grade 150 agloporite concrete were 65 units, and grade 400 - 62 units. Deformations of grade 150 concrete containing crushed granite were 73 units, and grade 400 - 92 units.

Apparently at this rate of freezing ( $t = -30^{\circ}\text{C}$ ) the segregation of ice which causes intense deconsolidation of concrete does not occur; the hydrostatic pressure of water is the principal disruptive factor here.

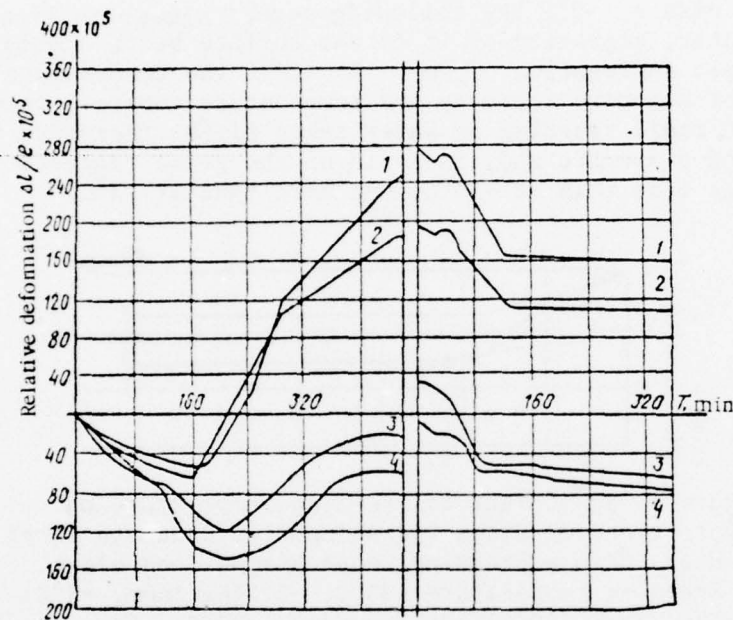


Figure 6.13. Deformation of Grade 400 Agloporite Concrete as a Function of Freezing Temperature. 1, 2, Deformations of samples at  $t = -7^{\circ}\text{C}$ ; 3, 4, The same at  $t = -3^{\circ}\text{C}$ .

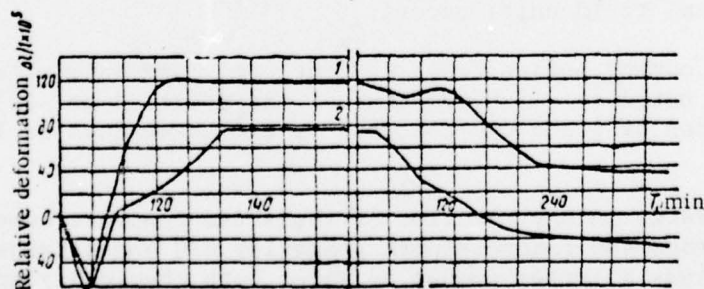


Figure 6.14. Effect of the State of the Aggregate on Deformations During Freezing. 1, Deformations of a concrete sample with wet agloporite; 2, Deformations of a concrete sample with dry agloporite.

Along with the fact that deformations in concretes of varied grades at 5 = -30°C are equal, their strength losses (15%) are equal since when ice segregation is absent high grades of concrete show better results. Deformations of samples of grades 150 and 400 concrete cured 1-3 days before freezing at various temperatures under normal conditions were studied later on. In grade 150 concrete expansion is no longer observed when it is cured 24 hours before freezing (Figure 6.15).

In this case at -3°C the following occur: slower cooling, greater bonding of water, migration of it to the surface being cooled, evaporation and microscopic segregation of ice. At -10°C the temperature gradient and evaporation of moisture increase and temperature compression occurs. At -20 and -30°C rapid freezing of water takes place; therefore it is not able to migrate and evaporate and, in spite of the great temperature compression, contraction is less than at -10°C, but more than at -3°C.

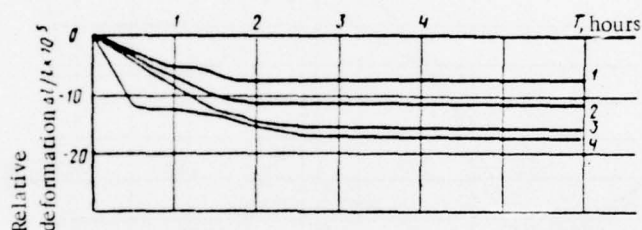


Figure 6.15. Effect of Freezing Temperature on Deformations of Grade 150 Agloporite Concrete Cured 24 Hours Before Freezing Under Normal Conditions.  
1, Freezing temperature -30°C; 2, The same, -5°C;  
3, The same, -10°C; 4, The same, -20°C.

A somewhat different picture is observed when grade 400 concrete is frozen at age one day. At -20°C the concrete expands approximately 11 units which follows brief contraction. Expansion is also noted at -10°C, but contraction is more protracted, a large amount of free water is bound and even though expansion occurs, it does not cause an increase in the initial dimensions (Figure 6.16). At -5°C no expansion at all is observed, and contraction equal to 15 units occurs.

Three-day curing before freezing completely prevents expansion. Contraction is noted at all temperatures, the greatest at -20°C. On the whole contraction of grade 400 concrete at age three days is less than grade 150.

The difference in the behavior of these two concrete compositions lies in that grade 400 concrete with a smaller W/C and a larger amount of cement paste binds a larger amount of water both chemically and by adsorption in cooling down to 0°C, and therefore contraction occurs basically due to shrinkage.

To conclude this examination of data on concrete deformations during freezing, let us cite the results of an experiment in which concretes containing various aggregates were compared. Concrete prisms were made

using volcanic slag, haydite, crushed limestone and granite, and metallic globules as aggregates. In examining these data we see that the greatest deformations in all series of samples occurred in concrete containing volcanic slag, and the least in concretes using metal globules (Figure 6.17). Thus, it was established that the heavy aggregate which differed from the mortar component in terms of deformability and the coefficient of temperature expansion resists expansion to a greater degree during freezing. This creates a concentration of stresses at the contact with the aggregate by destroying the concrete structure. In this case the advantage of light aggregate is confirmed by the results of compression, tensile and frost resistance tests on the concrete.

O. P. Mchedlov-Petrosyan and V. L. Chernyavskiy [43] also studied the effect of freezing on concrete deformation in their works. They measured deformations during freezing at  $-20^{\circ}\text{C}$  with concrete prisms  $10 \times 10 \times 30$  cm cured in metal forms at  $20 \pm 1^{\circ}\text{C}$  and a relative humidity of almost 90% for 0; 12; 24; 48; 60 and 72 hours. In this case some artificial stress on the tensometer membrane was recorded and a relative zero was selected; this is dictated by the necessity of recording not only expansion, but also contraction of the samples being tested. After stabilizing the volumetric transformations of concrete, the cooling chamber was shut down and its temperature slowly increased to  $20 \pm 1^{\circ}\text{C}$ ; this made it possible to follow the behavior of samples during thawing and record the residual strains.

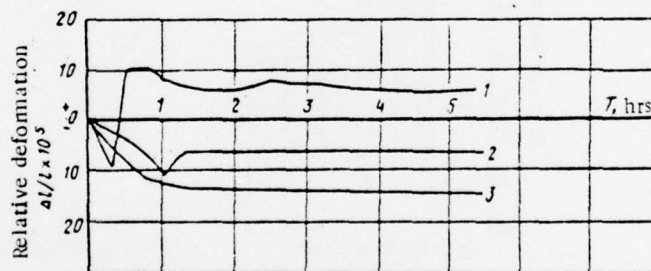


Figure 6.16. Effect of Freezing Temperature on the Deformation of Grade 400 Agloporite Concrete Cured 24 Hours Before Freezing Under Normal Conditions.  
1, Freezing at  $t = -20^{\circ}\text{C}$ ; 2, The same,  $-10^{\circ}\text{C}$ ;  
3, The same,  $-5^{\circ}\text{C}$ .

The effect of a sub-zero temperature on the change in the dimensions of concrete prisms cured for different periods of time under normal temperature-humidity conditions is shown in Figure 6.18. Concrete cooled without precuring exhibits maximum expansion after a certain contraction; the increase in the cooling time reduces the size of deformations. Under ordinary conditions the concrete hardening time affects the intensity of the developing formations such that the maximum rate of expansion (approximately 0.6 mm/m per hour) is observed in newly frozen concrete. This is due to the fact that the low strength coagulation structure of concrete demonstrates a minimal ability to resist internal stresses. During the first minutes of hardening only a small amount of water participates in the



chemical interaction with the cement, and the rest of it, adsorbed to a small degree by the comparatively coarse particles of the cement and aggregate, freezes near  $0^{\circ}\text{C}$ .

Precuring reduces the magnitude of relative deformations of concrete when it is subsequently frozen, because the coagulation-crystallization structure of the material is strengthened in the hydration process and the concrete begins to acquire elastic properties. By this time the liquid phase is represented by a considerably smaller amount of mineralized water, and the capillary-porous structure of the cement stone intensively adsorbs the liquid phase due to the large specific surface of the new formations (approximately  $200 \text{ m}^2/\text{g}$ ). A reduction in the magnitude and rate (approximately  $0.05 \text{ mm/m}$  per hour) of the volumetric changes of concrete hardening 60 and 72 hours down to cooling at  $+20 \pm 1^{\circ}\text{C}$  enables us to assert that the degree of strengthening of the structure determines the possibility of counteracting it by destructive stress at  $-20^{\circ}\text{C}$ .

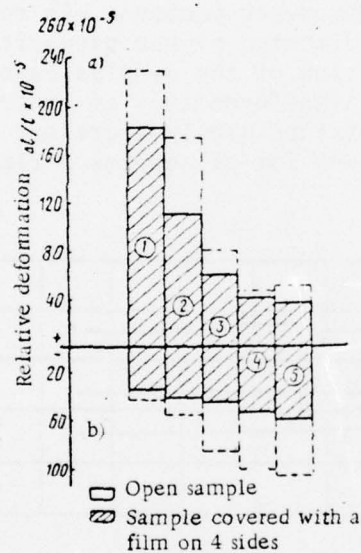


Figure 6.17. Deformations of Concrete at an Early Age as a Function of Type of Aggregate. a, At  $t = -20^{\circ}\text{C}$ ; b, Under dry air conditions at  $t = 19^{\circ}\text{C}$  and  $W = 70\%$ ; 1, Concrete containing volcanic slag; 2, The same, containing haydite; 3, Containing crushed limestone; 4, Containing crushed granite; 5, With metal globules instead of crushed stone.

The effect of frost on deformations of freshly poured concrete has been studied by A. I. Nevill as well. In contrast to the data cited on measuring linear deformations, he measured volumetric changes in concrete samples. He studied the increase in volumetric deformations [44] when freezing concrete at age up to 36 hours from the beginning of mixing it (Figure 6.19). A considerable reduction in the amount of concrete expansion is observed after hardening it at a normal temperature for 16 hours;

complete absence of hardening after 36 hours is also noted. His data and conclusions are in good agreement with those described previously.

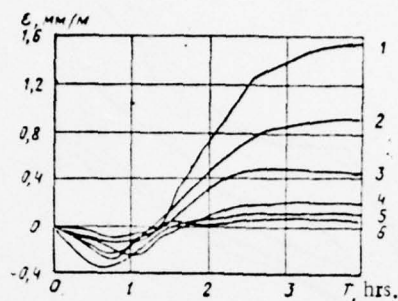


Figure 6.18. Change in Deformations of Concrete Prisms During Freezing as a Function of Precuring Time. For curves 1, 2, 3, 4, 5, 6 the time of precuring was 0; 12; 24; 48; 60; 72 hours respectively.

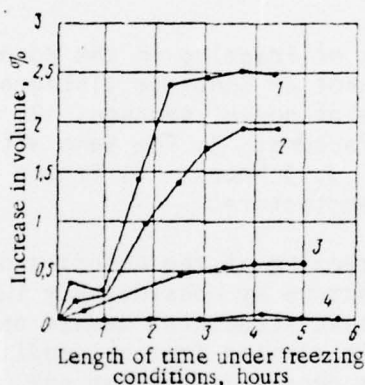


Figure 6.19. Effect of Precuring Time on the Increase in Volume of Concrete During Freezing. For curves 1, 2, 3, 4 the time of precuring was 4; 8; 16; 36 hours respectively.

The integral and differential porosity of cement stone and concrete was studied along with deformations using methods of mercury porometry and water absorption. The tests were conducted on samples  $7 \times 7 \times 7$  cm of concrete of composition 1:2.1:3.7 at a  $W/C = 0.58$ . The cement used was from the Belgorod Factory and crushed limestone was used as the coarse aggregate. Samples were frozen 3 days at  $-2$  and  $-20^{\circ}\text{C}$  at an early age (Table 6.4). Samples of mortar taken from the concrete were tested using the mercury depression method after 28 days of normal hardening and treatment with alcohol. Integral curves of pore distribution by size were plotted on the basis of these data (Figure 6.20). It can be seen from the drawing that the porosity of concrete decreases as the length of time it is precured before freezing increases. Samples frozen after 3 hours, i.e., during the cement setting period, demonstrated the greatest porosity. Calculations of pore volume by various radii were conducted on the basis of the integral curves.

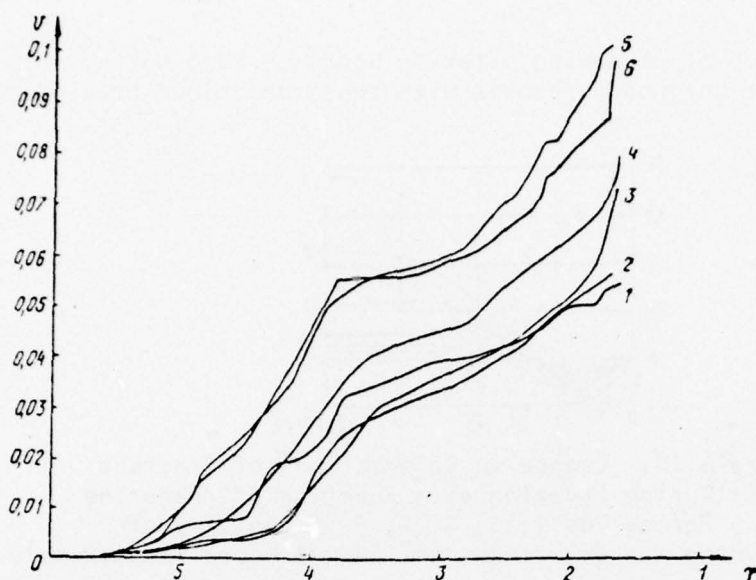


Figure 6.20. Effect of Freezing on the Porosity of the Mortar Component of Concrete (Integral Curves). 1, 28 days of normal storage; 2, Frozen 24 hours after manufacture; 3, The same after 12 hours; 4, 9 hours; 5, 3 hours; 6, Frozen immediately after manufacture.

As studies have shown, freezing of the cement stone in concrete at an early age disrupts its structure by considerably increasing the porosity of these materials. The greatest structural damage and increase in porosity (see Table 6.4) are observed in samples frozen immediately after preparation and especially in samples frozen before the end of setting of the cement.

As the time the concrete is precured before freezing increases, its structure is improved and porosity is noticeably reduced; when freezing concrete at age 24 hours there are almost no dislocations, and the pore volume approaches the pore volume in normally hardened concrete. In this case it should be noted that the greatest disruptions and weakening of the contact zone between the aggregate and mortar component occur at higher sub-zero temperatures ( $-2$ ,  $-5^{\circ}\text{C}$ ) due to the more favorable conditions for migration of moisture during slow freezing of the concrete.

As petrographic studies have shown, during early freezing of concrete the principal changes occur in its macrostructure in pores larger than  $1\ \mu$ . Similar data were obtained in determining sample porosity using the methods of water absorption and mercury porometry. When concrete is frozen immediately and 3 hours after preparation at  $20^{\circ}\text{C}$  a considerable increase in the volume of pores larger than  $1\ \mu$  is noted in the mortar component of the concrete. When freshly made concrete is frozen at  $-2^{\circ}\text{C}$  the pore content  $1 > r > 0.1\ \mu$  increases; this should lead to a deterioration in the strength properties of concretes frozen at an early age and to a considerable increase in their permeability and frost resistance compared to concretes frozen at an early age at  $-20^{\circ}\text{C}$ .



TABLE 6.4. EFFECT OF EARLY FREEZING OF CONCRETE ON ITS STRUCTURE

Hardening Conditions	Total porosity, cm <sup>3</sup> /g	Pore distribution by radii and their volume							
		$r > 10^1 \text{ \AA}$		$10^1 > r > 10^2 \text{ \AA}$		$10^2 > r > 10^3 \text{ \AA}$		$10^3 > r > 10^4 \text{ \AA}$	
		cm <sup>3</sup> /g	%	cm <sup>3</sup> /g	%	cm <sup>3</sup> /g	%	cm <sup>3</sup> /g	%
Frozen immediately after preparation at -20°C and hardened 28 days after thawing under normal conditions	0,07695	0,0159	20,7	0,0306	39,7	0,0209	27,2	0,00955	12,4
Frozen immediately after preparation at -20°C and hardened 28 days after thawing under normal conditions	0,0979	0,04929	50,3	0,0099	10,1	0,0181	18,5	0,02065	21,1
Frozen 3 hours after preparation at -20°C and hardened 28 days after thawing under normal conditions	0,1115	0,0494	44,4	0,0107	9,6	0,0226	20,2	0,0288	25,8
Frozen 9 hours after preparation at -20°C and hardened 28 days after thawing under normal conditions	0,0797	0,0298	37,5	0,0157	19,7	0,0167	21	0,01745	21,8
Frozen 12 hours after preparation at -20°C and hardened after thawing	0,0704	0,0168	23,8	0,0200	28,4	0,0134	19	0,02015	28,8
28 days under normal conditions									
Frozen 24 hours after preparation at -20°C and hardened after thawing for:									
28 days under normal conditions	0,05166	0,01046	20,3	0,00328	6,3	0,0285	55,2	0,00943	18,2
28 days under normal hardening	0,055	0,0205	37,2	0,0135	24,6	0,0148	26,9	0,0062	11,3

Commas indicate decimal points.

These conclusions are confirmed by testing appropriate samples for strength, frost resistance, gas and water permeability.

The kinetics of the structural formation and the ultimate structure of cement stone as well as its strength characteristics depend to a considerable degree on the mineralogical composition of the cement. The mineralogical composition of the cement acquires especially great significance when concreting under sub-zero temperature conditions.

In studying concrete porosity, cube-shaped samples were water saturated using the hydrostatic weighing method [58]. The volumes of the water absorbed by the samples frozen at various ages were determined. Gradients of sample porosity were established by analyzing the results. Conclusions which correspond with those set forth previously were obtained using this method, although only approximately so.

To more fully reveal and more clearly show the role of physical phenomena directly in the strength indicators of the concrete when it is frozen at an early age, our 1945 experiment was reproduced in expanded form in 1972 with repeated vibrations in the thawing or freshly frozen concrete with concrete mixtures of workable consistency containing two portland cements.

Concrete samples  $10 \times 10 \times 10$  cm (composition 1:2.1:3.7, W/C = 0.72, slump 2-3 cm) after preparation and placement of the mixture are transferred to a refrigeration unit immediately and after 4 and 6 hours. At  $-15^{\circ}\text{C}$  they cured 3 days, then some were tested after thawing, and some stored under normal conditions for up to 28 days. This test has again shown that repeated vibration during the thawing process of concrete before it acquires thixotropic properties raises strength 8-14% of  $R_{28}$  by 28 days of subsequent hardening. Concrete of the same composition not subjected to repeated vibration during 28 days thawing exhibited a reduction in strength by 10-39% of  $R_{28}$  (Table 6.5). Concrete containing grade 300 portland cement with a cement consumption of  $250 \text{ kg/m}^3$  was used in the experiment in 1945.

The test showed that when using workable concrete mixtures vibration may be carried out up to 6 hours, i.e., before the end of cement setting, after which the concrete structure has already become irreversible.

The workable concrete mixture was vibrated when placing it in the forms. Of the three series of concrete samples, one was stored under normal conditions, and two were exposed to freezing conditions (at  $-15^{\circ}\text{C}$  ...  $-25^{\circ}\text{C}$ ) soon after placing the concrete. The samples remained 3 days under freezing conditions, and then were brought into the laboratory. After thawing some of the samples were again vibrated.

The results shown in Table 6.6 were obtained after normal storage.

TABLE 6.5. EFFECT OF REPEATED VIBRATION OF CONCRETE  
AFTER THAWING ON ITS STRENGTH

Hardening conditions of concrete and time of sample vibration	Compression strength of concrete at age 28 days	
	Containing Belgorod cement	Containing Voskre- senskiy cement
Mixture vibrated immediately after placement in forms, then 28 days normal hardening of samples	<u>25,8</u> 100	<u>27,5</u> 100
Mixture vibrated immediately after placement, samples frozen and tested after 28 days of normal hardening	<u>18,8</u> 61,3	<u>24,4</u> 89,9
The same, but after thawing up to 4°C the samples were vibrated, then 28 days of normal storage	<u>27,8</u> 108	<u>30,3</u> 110
The same, the samples vibrated not immediately, but 4 hours after thawing up to 4°C	—	<u>31,4</u> 114
The same, but samples vibrated 24 hours after thawing	<u>24,5</u> 95	<u>24,9</u> 90,5
Mixture vibrated immediately after placement in forms, then again vibrated after 24 hours and stored 28 days under normal conditions (without freezing)	<u>25,7</u> 100	<u>30,2</u> 109,9
The same, but samples vibrated 6 hours after placing the mixture in forms.	<u>28,4</u> 110,1	<u>32,4</u> 117,9

Note. Numerator shows strength in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

It was established that repeated vibration of concrete at the instant it thaws imparts to it an increase in strength, and not a decrease, as in the case of freezing without repeated vibration before subsequent storage under normal conditions. These tests have convinced the author of the necessity of proposing a method for restoring the structure and strength of concrete frozen immediately after placement in the forms.

The method of restoring the strength of frozen concrete suggested by us may be used in a number of cases of construction practice (concreting of floors, roads, foundations under light equipment, etc.). This method may also be used to restore the strength of certain non-massive rubble and



concrete rubble masonry set into the ground. The cohesion of the mortar with the rubble after light vibration will subsequently increase on thawing.

Vibration of concrete during its thawing period when it acquires the ability to reconsolidate as freshly placed, eliminates structural damages. Therefore the strength is higher than in normally hardened concrete not exposed to freezing. Tests conducted in a Scientific Research Institute of Roads in 1948 confirmed the theoretical premises of the author and the possibility of introducing this method under certain road construction conditions.

TABLE 6.6. CONCRETE STRENGTH AFTER VARIED STORAGE

Storage conditions of the samples	Concrete strength at age			
	15 days		100 days	
	MPa	%	MPa	%
Normal storage conditions	9,6	100	11,6	100
3 days in freezing weather, then normal storage conditions	7,6	79,2	11,2	97
3 days in freezing weather, then normal storage conditions using repeated vibration after thawing	10,6	110,4	12	104

Commas indicate decimal points.

It can be seen from the experimental data cited in this chapter that premature freezing does not affect the properties of mortars and concretes in exactly the same way. Concretes, as is apparent from the tests, suffer more from early freezing. This difference becomes even more clear in evaluating the role of the freezing of masonry and concretes. If the role of mortar in masonry of stone of the correct form is comparatively small (it is rather a bed for distributing pressure from the brick), in concrete the cement mortar comprises the framework, the skeleton which determines its strength. This may be shown rather graphically in the example of the behavior of frozen brickwork and concrete at the instant of thawing.

The strength of brickwork depends mainly on the strength of the brick and to a lesser extent on the strength of the mortar. Therefore a 20% loss in strength by a plastic cement mortar subsequently has little effect on the supportive ability of the masonry. The necessary cohesion of the mortar and brick under the weight of the compressed brickwork will be fully ensured. Therefore with regard to methods of conducting concreting operations in winter there are arrangements which differ in principle from those ordinarily used in masonry. In conducting concreting operations any premature freezing of the concrete is strictly forbidden. Masonry, however, allows freezing and moreover as soon as possible after placing the mortar and brick or stone of the correct shape.

The traditional principles of masonry which have formed over the centuries have begun to be re-examined by builders beginning in the 1930's. Up to that time masonry work ceased with the onset of the first frosts, and in an extreme case it was conducted in spacious winter shelters.

In 1931 the Technical Specifications of the All-Union Trust for Construction of the Supreme Council of the National Economy authorized for the first time masonry work in winter without heated shelters, but with heated mortar and brick and with compulsory heating of the masonry, i.e., using the thermos method. Subsequent research and practice have shown that it is possible to forego the heating of the brick and masonry work. The Technical Specifications for winter construction authorized masonry work using the refrigeration method with a recommendation for warming the walls within the buildings (suggestion was developed by V. M. Medvedev at the Central Scientific Research Institute of Industrial Structures). Then, step by step, they finally switched to using the method of refrigerating the masonry after gradually ascertaining its behavior.

As early as 1934 in the reissued Technical Specifications for Winter Operation, placement using plastic mortar instead of placement "with a trowel" used at first, i.e., with a stiff mortar, was adopted on the suggestion of the author. Tests conducted by us in 1935 in the country laboratory of the Central Scientific Research Institute of Industrial Structures have made it possible to more soundly and boldly pose the question of the complete switch to masonry work with the refrigeration method using plastic mortars.

Plastic mortars have made it possible to increase the productivity of bricklayers, reduce the settling of walls, and increase the strength of masonry due to the superior cohesion of the mortar and brick and more favorable conditions for hardening later on.

Calculations carried out according to formulas of the dependency of masonry strength on brick and mortar strength show that under the most unfavorable freezing conditions for the masonry, its strength drops no more than 15% after 28 days. The strength of masonry of large and medium-size blocks in winter drops even less.

The tests of A. A. Shishkin and I. T. Kotov show that brick masonry built according to the refrigeration method (just as newly built masonry) thaws, its strength is approximately 50% of summer masonry at age one month. Then the strength of the masonry increases with time due to the hardening of the mortar.

Thus, the low percentage of mortar in the volume of the masonry and its comparatively limited role in developing strength make the use of masonry work with the refrigeration method permissible.

A completely different picture is observed in testing the strength of prematurely frozen concrete structures. The presence of a coarse aggregate in the concrete and the metal reinforcement in reinforced concrete causes still more imperfections during early freezing of structures.

The bonding strength of the mortar and coarse aggregate as well as the concrete and steel drops sharply during early freezing. In contrast to placing a stone of the correct shape, the concrete mixture must be placed in form-work.

Regardless of the prescribed form and dismantling periods of structures, freezing of concrete results in considerably greater strength losses than is the case in mortars, and even more so in masonry. Attempts to use the refrigeration method of concrete in structures have not justified themselves. Therefore the refrigeration method of concrete is forbidden by construction standards and regulations.

Regardless of the strength loss of concrete and reinforced concrete, premature freezing is not permissible according to the conditions for the use of the form-work and structures themselves. Frozen structures must not be stripped and loaded before the beginning of warm spring weather; this delays the implementation of all further construction operations.

These results of studies of premature freezing of concrete may be used in the solution of certain questions which arise in winter concreting practice. They represent the material using which it is possible to substantiate judgments of the temporary supportive ability of the frozen structure and the possibilities of correcting it in warm weather. Comparatively favorable results of laboratory tests cannot be used as the basis for tolerating the freezing of concrete at an early age. This is confirmed by the comparatively large number of corrections or complete replacement of structures frozen during winter operations.

#### Effect of Early Freezing on the Strength and Deformative Characteristics of Concrete.

It was necessary to study the deformative properties of concrete in order to fully elucidate the problem of the effect of sub-zero temperatures on the properties and structure of concrete frozen at an early age and then hardened at an above-zero temperature as well as to provide additional substantiation for the critical strength values cited previously. In conjunction with this Ye. G. Glazyrina at the Scientific Research Institute of Concrete and Reinforced Concrete studied the effect of freezing of concrete at an early age on such characteristics as the prism and cubic strength, initial modulus of elasticity, the coefficient of lateral deformation, volumetric deformations.

Prisms  $10 \times 10 \times 40$  cm and cubes  $10 \times 10 \times 10$  cm of concrete of a composition 1:1.4:2.4 with a cement consumption of  $500 \text{ kg/m}^3$  and a W/C = 0.4 were made for the tests. Portland cement from the "Bolshevik" Factory with an activity of 45 MPa was used as the binding agent. The inert materials used included crushed limestone with a grain-size of from 5 to 30 mm, quartz river sand with a  $M_{\text{size}} = 2.3$ .

One group of the samples was frozen immediately after preparation at  $-20^\circ\text{C}$ , the other frozen at the same temperature with a strength of 30% of the planned. After 3 days of exposure to sub-zero temperatures the samples



were transferred to a normal storage chamber, where they were hardened for 28 days. The control sample was hardened 28 days under normal conditions. Deformations of the concrete were measured with tensometers with a base of 100 mm glued onto the concrete samples being tested both laterally and longitudinally and they were recorded using automatic gauge AI-1. The strength and deformative characteristics of the concrete of the samples under study which were obtained from the test are shown in Table 6.7.

TABLE 6.7. EFFECT OF EARLY FREEZING ON THE STRENGTH AND DEFORMATIVE CHARACTERISTICS OF CONCRETE

Hardening conditions of the concrete	Series No.	Strength characteristics of the concrete					Deformative characteristics of the concrete	
		$R_{cube}$ , MPa	$R_{pr}$ , MPa	$\frac{R_{pr}}{R_{cube}}$	$\frac{R_{cube}^t}{R_{cube}^H}$	$\frac{R_{pr}^t}{R_{pr}^H}$	$E_{st} \cdot 10^{-3}$ , MPa	$\frac{E_{st}^t}{E_{st}^H}$
Hardening 28 days under normal conditions	1	45	33	0.73	—	—	28.1	—
	2	47	33	0.7	—	—	29.3	—
	3	49	34	0.7	—	—	29.6	—
	4	50.5	36	0.71	—	—	31.4	—
Frozen at $-20^{\circ}\text{C}$ immediately after preparation and then hardened 28 days under normal conditions	1	38.6	27	0.7	0.86	0.82	25.7	0.91
	2	40	30	0.75	0.85	0.91	27.3	0.93
	3	39	30	0.77	0.8	0.88	28.5	0.96
	4	41.5	30	0.72	0.82	0.83	28.6	0.91
Frozen with a strength of 30% of $R_{28}$ , then hardened 28 days under normal conditions	3	47.5	36	0.76	0.97	1	30	1
	4	52	36	0.7	1	1	29.8	0.95

Note.  $R_{cube}^H$ ,  $R_{cube}^t$  - Cubic strength of concrete normally hardened and subjected to freezing respectively;

$R_{pr}^H$ ,  $R_{pr}^t$  - Prism strength of the same concrete;

$E_{st}^H$ ,  $E_{st}^t$  - Static modulus of elasticity of compression of the same concrete.

Commas indicate decimal points.

It is apparent from the curve of the dependency of  $E_{long}$ ,  $E_{lat} = f(\sigma)$  plotted from the results of the tests (Figure 6.21) that the magnitudes of the longitudinal and lateral (plastic and absolute) linear deformations of concrete frozen at an early age are greater than the deformations at the control samples caused by identical axial compression stresses.

Thus, when concrete is frozen immediately after preparation the lateral linear deformations caused by compression stresses  $\sigma = 0.5 R_{pr}^H$  increased 11.4%, and at  $\sigma = 0.9 R_{pr}^H$  17.8%. The increase in lateral compression deformation is more significant - 33.3% at  $\sigma = 0.5 R_{pr}^H$  and 36.2% at  $\sigma = 0.9 R_{pr}^H$ .

The reduced resistance to the development of linear deformations of concrete frozen immediately after preparation under the compressive load can be easily explained from the point of view of established concepts of the effect of a sub-zero temperature on concrete at an early age.

It has been established by measuring deformations [39] that deconsolidation of the concrete mixture caused by the increase in the volume of water during freezing increases when concrete is exposed to a sub-zero temperature immediately after it is prepared. As the result of this condition of the formation of the concrete structure a further increase in crystallohydrates of new formations, their binding and formation into conglomerates and concretions are hindered. Under especially severe conditions the structure is formed when the cement stone contacts the coarse aggregate, since the formation of an air layer around the aggregate is possible. All this results in the fact that by 28 days of subsequent hardening at an above-zero temperature the concrete does not acquire the planned strength. Concrete frozen immediately after preparation which is weakened compared to normally hardened concrete demonstrates a reduced modulus of elasticity. The drop in the initial modulus of elasticity is 10-12%, and that of the cubic and prism strength 15-20 and 10-17% respectively.

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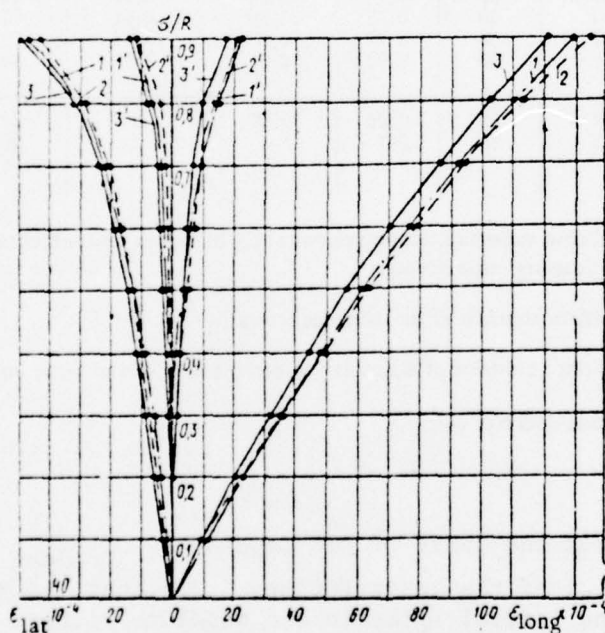


Figure 6.21. Linear Absolute and Plastic Deformations as a Function of Axial Compression Stresses in Concrete. 1, In concrete stored under normal conditions; 2, Frozen at critical strength; 3, Frozen immediately after preparation; 1', 2', 3', Plastic deformations of the same concretes.

When concrete at the critical strength (30% of the planned strength for a given grade of concrete) is frozen, the amount of free water drops considerably during the freezing period, and the structure is molded to such a degree that the walls of the pores and capillaries are able to resist the pressure of the expanding free water [28, 39].

As the result of deformations, expansion is not observed, the structure is not damaged, the concrete loses neither prism nor cubic strength later on and differs insignificantly (0-5%) with regard to the modulus of elasticity from normally hardened concrete. This is good agreement with data obtained previously concerning the fact that the dynamic modulus of elasticity of concrete frozen at the critical strength does not drop either.

A comparison of the dependencies of longitudinal linear deformations of concrete subjected to the action of a sub-zero temperature at an early age and of a concrete under normal storage  $E_{\text{long}} = f(\sigma/R_{\text{pr}})$  shows (Figure 6.22) that the absolute longitudinal deformations of concrete frozen immediately after preparation are less than the corresponding deformations of concrete under normal storage (at  $\sigma/R_{\text{pr}} = 0.5$  the drop is 10%, and at  $\sigma/R_{\text{pr}} = 0.9$  it is 7%). Lateral deformations of concrete frozen immediately after preparation are practically equal to deformations of concrete under normal storage.

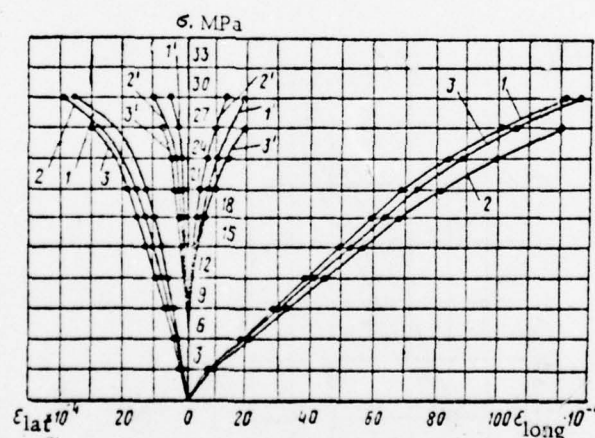


Figure 6.22. Linear Absolute and Plastic Deformations as a Function of the Level of Axial Compression Stresses in the Concrete. 1, Concrete under normal storage; 2, Frozen at critical strength; 3, Frozen immediately after preparation; 1', 2', 3', Plastic deformations of the same concretes.

The plastic deformations of the concretes tested vary in the following manner. The concrete frozen immediately after preparation exhibits less longitudinal plastic deformation than the concrete under normal storage and that frozen at the critical strength. Its lateral plastic deformation



is practically equal to the deformation of concrete under normal storage. A drop in plastic deformations signifies some loss in plastic properties which has occurred during the freezing process of the concrete.

These bonds are not completely restored during subsequent hardening at an above-zero temperature, the contact with the coarse aggregate remains disrupted, and the material becomes more brittle. This is indicated in particular by the nature of the change, according to the load and the volume of the sample of concrete frozen at an early age.

As can be seen from Figure 6.23 the volume of such a concrete drops continually down to failure. No increase in the volume at the boundary of  $R_T^V$ , just as in concrete under normal storage, is observed. Cement stone has this same nature of the change in volume which differs in principle from concrete under normal storage.

This analogy in the nature of the change of a volume of cement stone in concrete frozen immediately after preparation under load may be explained by the special features of the structure of the latter. It may be assumed that the load is transferred mainly to the mortar portion due to the contacts which have been weakened as the result of the effect of a sub-zero temperature with the coarse aggregate in frozen concrete. The mortar portion of the concrete frozen immediately after preparation in turn demonstrates imperfections.

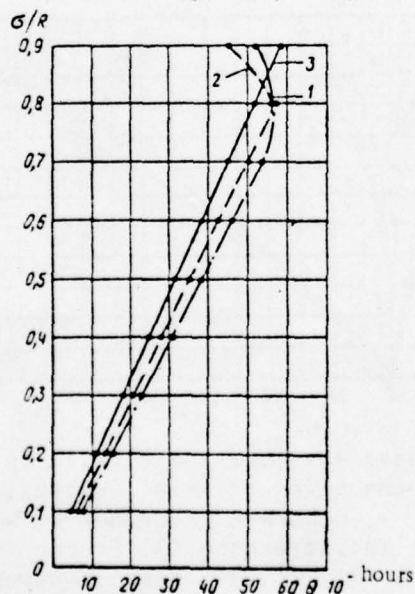


Figure 6.23. Volumetric Deformations as a Function of the Level of Axial Compression Stresses in Concrete. 1, Concrete under normal storage; 2, Frozen at the Critical Strength; 3, Frozen immediately after preparation.

It is known that in lean mortars with great porosity the solidity is not disrupted after freezing, and the same properties may be produced in them that are produced during hardening under normal conditions.

In this case the mortar component of a concrete contains a great deal of cement, therefore a disruption of the physical-mechanical properties and a partial loss of plasticity are observed, and possibly therefore the change in its volume suggests cement stone. The change in the differential coefficient of lateral deformation of concrete frozen immediately after manufacture also suggests cement stone by nature (Figure 6.24).

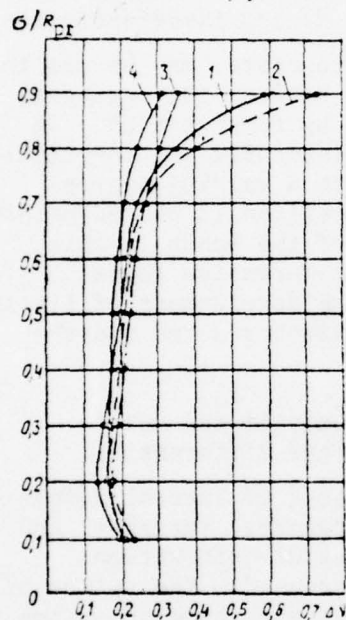


Figure 6.24. Differential Coefficient of Lateral Deformation  $\Delta v$  as a Function of the Level of Axial Compression Stresses in Concrete. 1, Normally hardened concrete; 2, Frozen at the critical strength; 3, Frozen immediately after preparation; 4, Cement stone.

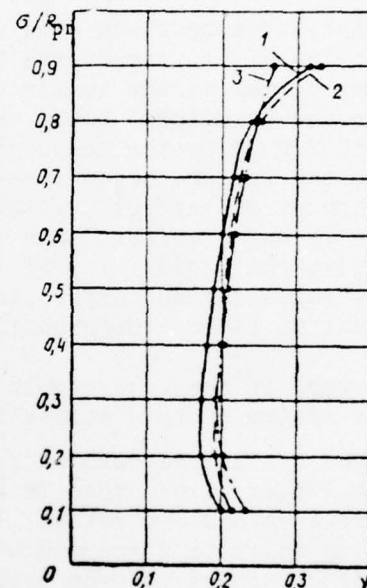


Figure 6.25. Coefficient of Lateral Deformation as a Function of the Level of Axial Compression Stresses in the Concrete. 1, Normally hardened concrete; 2, Frozen at the critical strength; 3, Frozen immediately after preparation.

In absolute value  $\Delta v$  of concrete exposed to the effect of a sub-zero temperature up to the 0.75 stress level is higher than in concrete normally hardened and frozen at the critical strength. As the load increases in these two concretes a substantial increase in the differential coefficient of lateral deformation which signifies the beginning of micro-failure begins. This increase is practically absent in concrete frozen immediately after preparation, but a small increase in  $\Delta v$  is observed just as in cement stone up to failure.

The coefficient of lateral deformation is another value which characterizes the deformative properties of concrete and which is used to design reinforced concrete structures. The coefficient of lateral deformation of all of these concretes as a function of the level of stresses is shown in Figure 6.25.

It can be seen from the graph that at load levels up to  $0.75 R_{pr}$  the coefficient of lateral deformation of concrete frozen immediately after preparation is greater than in normally hardened concrete. At a load equal to  $0.2 R_{pr}$  the difference in the coefficient of lateral deformation is 17% on the average. The increase in the coefficient of lateral deformation up to  $\sigma/R_{pr} = 0.75$  of concrete frozen immediately after preparation, in comparison with normally hardened concrete, may be due to the weakening of its structural bonds (principally between the aggregate and cement stone) as the result of deconsolidation by frost action. In this case the structural bonds which are oriented laterally and longitudinally with regard to the compressive force weaken to a varying degree. But since the failure of concrete under axial compression is caused mainly by development of lateral deformations, weakening of the bonds in this direction is more manifest than along the line of compressive force. Accordingly, the resistivity of this concrete to the development of linear tensile strains during compression is to a large extent reduced and the coefficient of lateral deformation increases.

However, if the concrete is deformed as a deconsolidated multi-component system up to a stress level of  $0.75 R_{pr}$  (the differential coefficient of lateral deformation and the coefficient of lateral deformation with larger values than in normally hardened concrete increase, and the external volume decreases), the special features of deformation inherent in concrete disappear when the load is increased. The volume of the sample continues to drop until failure, and no sharp increase in the coefficient of lateral deformation is observed. We may assume that the primary load is transmitted to the mortar component only in view of the ultimate weakening of the bond between the aggregate and cement stone. In terms of the nature of deformation under load, the mortar component which has partially lost its plastic properties due to frost action approximates cement stone. This is also indicated by the external nature of the failure of samples frozen immediately after preparation. Brittle failure with the formation of longitudinal cracks through the entire height of the sample is observed in this concrete, similar to a model component system.

If the special features of brittle material are taken into consideration, it may be expected that concrete frozen immediately after preparation and then hardened under normal conditions will be distinguished by its low resistance to tension and shock, and great sensitivity to local stresses. These special features of deformation must be considered in those cases in which the concrete is frozen soon after preparation, contrary to concreting principles. With regard to concrete frozen at the critical strength, its lateral and longitudinal, absolute and plastic deformations are nearly equal to deformations of concrete stored under normal conditions.



The characteristics of deformation (change in the coefficient of lateral deformation, external volume of the sample) in concrete frozen at the critical strength are the same as in normally hardened concrete.

Thus, in terms of its strength and deformative properties, concrete cured up to the critical strength before freezing does not differ from normally hardened concrete. Therefore the freezing of concrete may be permitted only after it has reached the critical strength which is differentiated depending on the grade of the concrete which ensures its normal operation in the structure later on.

#### Hardening of Concrete at Sub-Zero Temperatures.

As was noted previously, the problem of hardening of concrete at sub-zero temperatures has been little studied. There are only a few data [19, 23, 32, 83] on the hardening of concrete in freezing weather. Hitherto, the mechanism of hardening has not been studied. Therefore the questions of the theory of concrete hardening in freezing weather were examined in detail in Chapters 1 and 2 and at the beginning of Chapter 6.

In conjunction with the published appearance of the opinion that after steam curing concrete hardens at temperatures down to  $-30^{\circ}\text{C}$ , we studied this question still more at the Scientific Research Institute of Concrete and Reinforced Concrete. It is of practical importance in establishing in winter the delivery strength of concrete in prefabricated articles. Calculation of the gain in strength of concrete in construction in permafrost regions may also return a great economic effect to the economy. Cast in situ concrete in contact with permafrost soils is used in large amounts in erecting foundations and underground facilities. The special feature of the conditions for hardening concrete in these regions lies in the fact that during operation the facilities are always at the temperatures of the frozen ground which vary from  $-0.1$  to  $-5^{\circ}\text{C}$ .

Together with experiments under laboratory conditions, the author participated in studies of concrete hardening under permafrost conditions in Vorkuta and Norilsk. Special chambers and underground laboratories in which the temperatures of natural frozen ground were constantly maintained were used for these purposes.

In Vorkuta, concrete samples stored there up to age 7 months were placed in contact with permafrost ground by a department of the All-Union Scientific Research Institute for the Construction of Trunk Pipelines and studied at various times after manufacture [6, 35]. Samples  $10 \times 10 \times 10$  cm with and without 2% calcium chloride added as a complex antifreeze agent were placed in permafrost soil, the temperature of which varied from  $-0.9$  to  $-2.7^{\circ}\text{C}$ . Samples containing portland cements of grade 300 and 500 were placed in the ground after prehardening under normal conditions for 3 hours, 1, 3 and 7 days. Some of the results of these tests are shown in Table 6.8.

As is apparent from these data, depending on the activity of the cement and the W/C at age one month, the concrete without the additive which was exposed to freezing conditions soon after manufacture acquired

from 38 to 69% of the  $R_{28}$  strength of normal hardening. When calcium chloride and the complex agent were added to the concrete, it increased to 86-90%. After 3 days of normal hardening the concrete acquires 69-83% of the  $R_{28}$  strength by age one month. When a small amount of the chemical agents are added, concrete in permafrost soil acquires a strength above that of the established grade with the passage of time (up to 7 months). The addition of such agents as calcium chloride cannot essentially disrupt the permafrost structure due to their rapid interaction with the cement minerals.

TABLE 6.8. INCREASE IN THE STRENGTH OF CONCRETE AT FROM -0.9 TO -2.7°C DEPENDING ON PRELIMINARY CURING AND CHEMICAL ADDITIVES

Preliminary curing under normal conditions, days	Concrete strength after curing in contact with permafrost soil					
	Without additive		With added $\text{CaCl}_2$		Complex additive NKM	
	1 mo.	7 mos.	1 mo.	7 mos.	1 mo.	7 mos.
Grade 200 concrete of composition 1:1.85:3.85 containing grade 500 cement, W/C = 0.5 (cement consumption 340 kg/m <sup>3</sup> )						
0,1	15,3	17,9	19,1	22,6	17,7	25,1
	69	80	86	101	79	112
1	15,6	21,1	18,5	22,4	18,4	24,1
	70	95	83	100	82	108
3	18,6	23,6	17,7	23,2	18,2	23,8
	83	106	79	104	85	107
7	20,4	25	20,6	26,1	19,5	25,6
	92	112	92	116	87	115
Grade 150 concrete of composition 1:1.85:3.95 containing grade 300 cement, W/C = 0.56 (cement consumpt. 340 kg/m <sup>3</sup> )						
0,1	5,5	5,7	13,2	13,1	14,9	17,2
	38	39	90	90	102	118
1	6,8	10,5	13,7	16,2	12,4	19,3
	47	72	94	111	85	132
3	10	11,3	13,5	14,3	12,9	13,1
	69	77	92	98	88	90
7	12	12,6	14,8	16,6	13,2	14,5
	82	86	101	114	90	99

Note. Numerator shows absolute values of compression strength, MPa; denominator - % of strength of  $R_{28}$  of concrete without additives.

Commas indicate decimal points.

Figure 6.26 shows the results of tests on samples of concrete without added chemicals which were made using grade 500 (curves 1, 2, 3, 4) and grade 300 (curves 5, 6, 7, 8) portland cement. As can be seen from the

figure, the gain in strength continues for one year and reaches 50% of the rated strength under the most unfavorable conditions. By comparing these data with those cited in Table 6.8, we may conclude that it is feasible to add chemical agents when placing concrete in permafrost soil. After obtaining these results, studies were conducted in the permafrost (underground) laboratory in Norilsk by the Norilsk Department of the Krasnoyarskiy Scientific Research Institute of Industrial Planning and Construction.

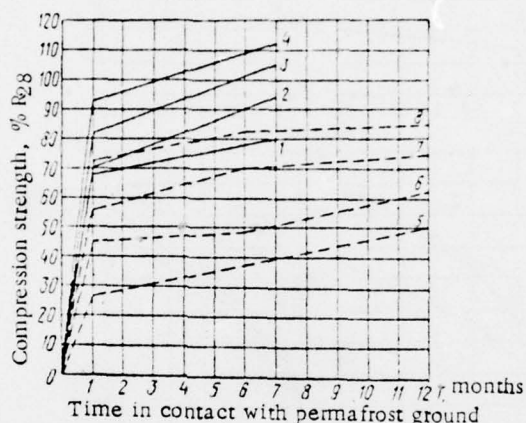


Figure 6.26. Increase in Strength of Grade 200 Concrete Containing Various Cements in Contact with Permafrost Ground (Vorkuta). 1, 5, Concrete frozen immediately after preparation; 2, 6, Frozen under normal conditions with 24 hours of curing; 7, The same, 3 days; 4, 8, The same, 7 days.

On the basis of these results and at the suggestion of the author, in constructing pile foundations builders have abandoned electrical heating and are changing to the simpler method of placing concrete with sodium nitrate, potash or calcium chloride added in small amounts. This has saved a great deal of money as well as electrical energy.

Figure 6.27 shows the characteristics of hardening of concrete in samples placed in permafrost soil in underground frozen chambers in Norilsk. Samples of concretes of varying compositions, including those containing a small amount of chemical additives, are cured for several months in chambers located underground at a depth of 8 and 15 m.

Work [3] examines the increase in strength of cement stone, mortar and concrete at  $-2$ ,  $-5$ ,  $-10$  and  $-20^{\circ}\text{C}$  for which were used portland cements from the Belgorod and Voskresenskiy Factories. The concrete mixture was prepared with a  $W/C = 0.5$  containing crushed agloporite and sand. The samples were frozen immediately after preparation and after 24 hours. The results obtained are similar, therefore a diagram showing the data from testing concrete containing just Belgorod cement is cited (Figure 6.28). These results of the study of hardening of agloporite concrete at sub-zero temperatures are in good agreement with the test data and conclusions made for concrete containing dense aggregates.



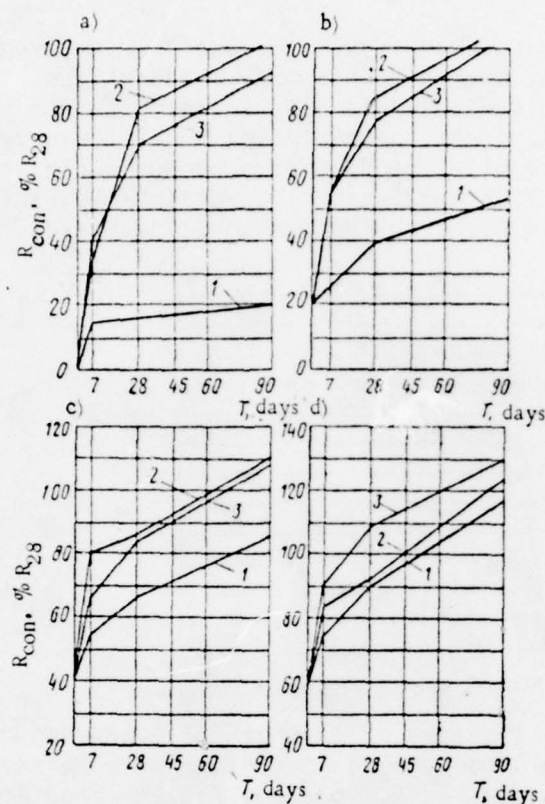


Figure 6.27. Increase in the Strength of Grade 300 Concrete in Contact with Permafrost Soil at  $-3...-4^{\circ}\text{C}$ . a, 0.1 days precuring under normal conditions; b, The same, 1 day; c, The same, 3 days; d, The same, 5 days; 1, Concrete without added chemicals; 2, Concrete with 3%  $\text{NaNO}_2$  + 0.2% SLW added; 3, The same, with 1.5%  $\text{NaNO}_2$  + 1.5%  $\text{CaCl}_2$  + 0.2% SLW added.

Tests in which samples were cured in a freezing chamber were conducted previously to check the value of preliminary curing before the beginning of freezing and the fineness with which the cement was ground for the hardening of concrete at  $-5^{\circ}\text{C}$  (with variations from  $-4$  to  $-6^{\circ}\text{C}$ ). The concrete samples contained two portland cements with a consumption of  $250 \text{ kg/m}^3$  each of mixtures with a consistency of 120 at a  $\text{W/C} = 0.5$ . One series of samples was placed in the chamber at  $-5^{\circ}\text{C}$  immediately after preparation, the second after they were cured at  $15^{\circ}\text{C}$  for 40 hours. The samples were cured in the freezing chamber for 180 days. Table 6.9 shows data on the gain in strength by the concrete at  $-5^{\circ}\text{C}$ .

As can be seen from the table, increased fineness of grinding factory cements considerably increased the rate of concrete strength gain. Precuring for 40 hours at  $15^{\circ}\text{C}$  exerted an even greater effect. In the case in which the hydration of cement with additional grinding achieved considerable development, subsequently this strength of the concrete increased 20-24%, or by 9.4-9.8 MPa at  $-5^{\circ}\text{C}$  for 5 months. The relative increase in strength was approximately the same for cements with and without additional grinding. Testing shows that the water content in the concrete dropped as

the result of the initial hydration of cement. The processes of cement hydration and gain in strength by the concrete were subsequently intensified in freezing weather.

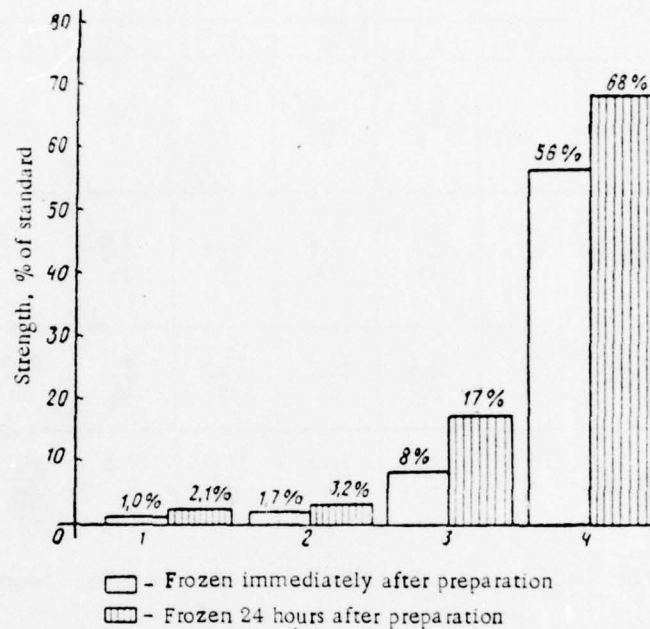


Figure 6.28. Diagram of the Increase in Strength of Agloporite Concrete Frozen at an Early Age Exposed to Freezing Conditions (Containing Belgorod Cement at a W/C = 0.5). 1, Frozen at  $t = -20^{\circ}\text{C}$ ; 2, At  $t = -10^{\circ}\text{C}$ ; 3, At  $t = -5^{\circ}\text{C}$ ; 4, At  $t = -2^{\circ}\text{C}$ .

Special tests [18, 32, 34] were conducted at a laboratory of the Scientific Research Institute of Concrete and Reinforced Concrete to study the hardening of concrete at a sub-zero temperature after it had achieved a certain strength under normal conditions. As the result it was established that at sub-zero temperatures cement hydration which has already begun, and as a result, the gain in strength by concrete, is more intense than in a freshly made state. In this case the fact that the hardening continues at temperatures below  $-10^{\circ}\text{C}$  is of interest (Table 6.10).

In order to develop recommendations for establishing the delivery strength of concrete of articles shipped to building sites in winter, L. A. Malininaya, I. M. Frenkel, A. S. Dmitriyev and the author conducted special studies of the effect of various temperatures on the intensity of subsequent hardening of a steam cured concrete. For this purpose tests were made at a constant sub-zero temperature of  $-20$ ,  $-10$  and  $-5^{\circ}\text{C}$  and with the temperature changing from  $-5$  to  $5^{\circ}\text{C}$  over 24 hours as well as under normal conditions. After steam curing the samples were placed in a freezing chamber at the temperatures indicated above. Before the test they were heated 4-5 hours at  $18-20^{\circ}\text{C}$ . Different cements were chosen for the tests and the concrete was frozen at a varying strength after steam curing.

TABLE 6.9. HARDENING OF CONCRETE AT  $-5^{\circ}\text{C}$  FOR 180 DAYS

Curing conditions	Cement preparation	Concrete strength limit at $-5^{\circ}\text{C}$ at age, days							
		28		90		180		28 days of normal hardening	
		V	B	V	B	V	B	V	B
Immediately into a cooling chamber at $-5^{\circ}\text{C}$	Without addit. grinding	$\frac{2.3}{6}$	$\frac{5.2}{15}$	$\frac{6}{17}$	$\frac{5.9}{17}$	$\frac{6.6}{18}$	$\frac{5.9}{17}$	$\frac{35.8}{100}$	$\frac{34.9}{100}$
	With additional grinding	$\frac{7.7}{16}$	$\frac{7.7}{19}$	$\frac{9.9}{20}$	$\frac{13.2}{32}$	$\frac{12.9}{26}$	$\frac{17.5}{43}$	$\frac{48.9}{100}$	$\frac{40.6}{100}$
40 hours curing at $15^{\circ}\text{C}$ , then at $-5^{\circ}\text{C}$	Without addit. grinding	$\frac{16.7}{47}$	$\frac{21.1}{60}$	$\frac{21.7}{61}$	$\frac{24.1}{69}$	$\frac{25.4}{71}$	$\frac{27.9}{80}$	$\frac{35.8}{100}$	$\frac{34.9}{100}$
	With additional grinding	$\frac{27.4}{56}$	$\frac{29.3}{72}$	$\frac{31.5}{65}$	$\frac{37.8}{93}$	$\frac{37.2}{76}$	$\frac{38.7}{95}$	$\frac{48.9}{100}$	$\frac{40.6}{100}$

- Notes: 1. Numerator indicates concrete strength in MPa; denominator - in % of  $R_{28}$ .
2. V - Portland cement from the Voskresenskiy Factory, B - Portland cement from the Belgorod Factory.
- Commas indicate decimal points.

It is apparent from Table 6.11 which was compiled from data from one of the tests that when storing samples at  $-20^{\circ}\text{C}$  there is either no increase in strength at all by age 28 days or it is very insignificant. As the temperature approaches zero, the intensity of the increase in strength of the steam cured concrete rises in time, and the strength deficit compared to the rated strength drops. At  $\pm 5^{\circ}\text{C}$ , steam cured concrete nearly reached its rated strength (97-100%) after 28 days, but its absolute value was nevertheless lower than when storing samples in a normal storage chamber for the entire period of time. After curing at  $-10^{\circ}\text{C}$  the strength of concrete increased 10% not only for 28 days, but also for 3-7 days compared to that of samples immediately after steam curing. At  $-5^{\circ}\text{C}$ , the strength of concrete containing Belgorod cement increased 16.5%. At  $-5^{\circ}\text{C}$ , a somewhat lower increase in strength was obtained for concrete containing Zdolbunovskiy cement, and at  $-10^{\circ}\text{C}$  almost no increase in strength was noted.

In order to give a more complete answer to the question of hardening of steam cured concrete at sub-zero temperatures, concretes were studied which contained other cements with a broader range of water-cement ratios. These studies were conducted at temperatures of subsequent hardening of steam cured concrete in freezing chambers of  $-20$ ,  $-15$  and  $-5^{\circ}\text{C}$  and a low above-zero temperature  $6-8^{\circ}\text{C}$ .



TABLE 6.10. INCREASE IN THE STRENGTH OF CONCRETE AT A SUB-ZERO TEMPERATURE DEPENDING ON TEMPERATURE AND STRENGTH OF CONCRETE AT THE INSTANT OF FREEZING

Strength of concrete before freezing, % of $R_{28}$	Increase in concrete strength in % after 28 days at, °C				
	0	-2	-5	-10	-20
0	50-60	20-30	5-10	1-3	1
5-10	40-60	30-40	15	3-5	2-4
15-20	50-70	45-50	20	15	10
30-50	—	—	15	10	8

TABLE 6.11. EFFECT OF OUTSIDE AIR TEMPERATURE ON THE HARDENING OF STEAM CURED CONCRETE

Cement	Temperature in the chamber when storing the concrete after steam curing, °C	Concrete strength after steam curing and subsequent storage in a freezing chamb.					Strength of conc. not steam cured after 28 days of normal storage
		1	3	7	14	28	
From the Belgorod Fact., W/C = 0.5	20	28,6	34,3	35	36	46,9	38,9
	(under normal hardening cond.)	73,5	88	90	92	120	100
	from +5 to -5	28,4	28,8	40	35,5	37,8	
		73	74	102	91,5	97	
	-5	30,4	30,3	36,1	35,6	35,1	
		78	78	92,5	91,5	90	
	-10	28,6	31,4	34,9	33,3	32,6	
		73,5	81,5	89,5	85,5	84	
	-20	25,2	29,3	31,9	27,6	31,8	
		65	75	82	82	80,5	
From the Novozdolbunovskiy Factory, W/C = 0.5	20	32	33,4	40,7	42,6	39,2	36,8
	(under normal hardening cond.)	87	91	111	116	107	100
	from +5 to -5	—	26,3	32,1	27,2	36,9	
		—	71,5	87	74	100	
	-5	—	26,2	31	26,9	31,2	
		—	71	84,5	73,5	85	
	-10	—	24,6	25,3	26,1	—	
		—	67	68,5	71	—	
	-20	—	24,4	23,2	25,2	28,7	
		—	67	63,5	68,5	78	

Note. Numerator shows strength in MPa; denominator in % of  $R_{28}$ .  
Commas indicate decimal points.

TABLE 6.12. CHANGE IN THE STRENGTH OF STEAM CURED CONCRETE WHEN SUBSEQUENTLY PLACED IN A FREEZING CHAMBER WITH A TEMPERATURE OF  $-20^{\circ}\text{C}$

Cement	W/C	Strength*			Strength* at $-20^{\circ}\text{C}$ after, days				
		4-5 hours after steam curing	28 days after steam curing	At age 28 days under normal hardening	1	3	7	14	28
Containing portland cement From the Novo-Zdolbunovskiy Factory	0,4	$\frac{32,7}{77}$	$\frac{44,2}{103}$	$\frac{42,7}{100}$	$\frac{37,3}{87}$	$\frac{35,7}{83}$	$\frac{35,6}{83}$	$\frac{29,9}{70}$	$\frac{35,9}{84}$
	0,6	$\frac{17,4}{52}$	$\frac{31}{92}$	$\frac{33,8}{100}$	$\frac{20,2}{60}$	$\frac{19,1}{57}$	$\frac{22,2}{66}$	$\frac{20,5}{61}$	$\frac{21,5}{61}$
Containing portland cement from the "Spartak" Factory	0,4	$\frac{24,5}{65}$	$\frac{38}{101}$	$\frac{37,8}{100}$	$\frac{29}{77}$	—	$\frac{31,5}{83}$	$\frac{29}{77}$	$\frac{30,1}{80}$
	0,6	$\frac{13,9}{50}$	$\frac{25,4}{91}$	$\frac{27,8}{100}$	$\frac{13,5}{49}$	—	$\frac{17,2}{62}$	$\frac{16}{58}$	$\frac{16,2}{59}$
Containing slag portland cement from the Kosogorskiy Factory	0,4	$\frac{31,4}{76}$	$\frac{53,2}{129}$	$\frac{41,1}{100}$	$\frac{31,3}{76}$	$\frac{36,4}{88}$	$\frac{31,8}{77}$	$\frac{34,6}{84}$	$\frac{34,2}{83}$
	0,6	$\frac{18,7}{69}$	$\frac{34,1}{126}$	$\frac{27,1}{100}$	$\frac{18,2}{67}$	$\frac{18,2}{67}$	$\frac{17,9}{66}$	$\frac{18,3}{67}$	$\frac{18,4}{67}$
Containing portland cement from the Mikhaylovskiy Factory	0,4	$\frac{21,9}{83}$	$\frac{33,7}{128}$	$\frac{26,4}{100}$	$\frac{27,5}{89}$	$\frac{23,7}{90}$	—	$\frac{20,4}{77}$	$\frac{21,9}{83}$
	0,6	$\frac{11,8}{75}$	$\frac{19,8}{126}$	$\frac{15,7}{100}$	$\frac{11,8}{75}$	$\frac{10,3}{66}$	—	$\frac{11}{70}$	$\frac{10,4}{66}$

\*Numerator shows strength of concrete in MPa; denominator in % of  $R_{28}$ .  
Commas indicate decimal points.

Steam cured concrete hardened at  $-20^{\circ}\text{C}$  was produced using portland cements from Novo-Zdolbunovskiy, Mikhaylovskiy, "Spartak" Factories and slag portland cement from the Kosogorskiy Factory. The concretes containing these cements were prepared with a water-cement ratio of 0.4 and 0.6. After forming, the samples were cured 1-5 hours and then steam cured as follows: rise in temperature - 3 hours; isothermic curing - 6 hours at  $80^{\circ}\text{C}$ , then natural cooling in a chamber. Only samples containing cement from the "Spartak" Factory which were steam cured 2 + 8 hours followed by natural cooling were excepted. The maximum steam curing temperature was

the same. After steam curing and cooling (4-5 hours) the samples were tested for strength, and the control samples were placed in a freezing chamber with a temperature of  $-20^{\circ}\text{C}$ . The samples were compression tested after a specific time in the freezing chamber. Before the test they were heated 4-5 hours at  $18-20^{\circ}\text{C}$ .

Table 6.12 shows the results of tests from which it is apparent that the strength of concrete varies unequally after freezing at  $-20^{\circ}\text{C}$  for 28 days. In some tests it remains as before, in others it increases or drops 2-11%. Ordinary deviations of the indicators of strength on the average of 7-11% were observed in either direction. The length of time under freezing conditions (from 1 to 28 days) had no substantial effect on the strength of samples of the same series. Consequently, there was no increase in strength for 28 days at  $-20^{\circ}\text{C}$ . At the same time the strength of the steam cured concrete 28 days in the normal hardening chamber increased on the average 30-40%. Some increase in the strength of concrete frozen 1, 3, 7, 14 and 28 days compared with that tested immediately after steam curing clearly occurs not as the result of its hardening at  $-20^{\circ}\text{C}$ , but during the freezing and thawing periods of the samples before the test. The data shown in Table 6.12 indicates that hardening of steam cured concrete at  $-20^{\circ}\text{C}$  practically ceases.

Concomitant with laboratory tests, additional tests were conducted using the same procedure in Krasnoyarsk and in Moscow to determine the gain in strength by the concrete under natural winter conditions. The only difference consisted in that the concrete samples were prepared using different portland cements (from the Novorossiyskiy and Belgorod Factories) and the thawing time before testing the samples after exposure to freezing weather was 20 hours. No samples were more than 28 days under freezing conditions. The temperature during this period varied from  $-15$  to  $-20^{\circ}\text{C}$  for the first two weeks, and then increased to  $-10^{\circ}\text{C}$  and higher. These tests, just as the preceding ones, show that the strength of steam cured concrete when it is cured in freezing weather from 3 to 28 days does not significantly change. However, the strength of concrete after 3 days under freezing conditions was 10-20% higher than the strength of the concrete immediately after steam curing. In this case the strength of the concrete increased not during freezing weather, but during the period of thawing and subsequent exposure to an above-zero temperature which was on the average  $20^{\circ}\text{C}$  before the experiment (approximately 20 hours). This is satisfactorily confirmed by testing samples at age 28 days, but thawed 4 hours, not 20 as in the preceding test. Difference of strength between the results of testing samples thawed 4 and 20 hours is 8 to 21%; this nearly coincides with the strength increase in concrete after 3 days in freezing weather compared to the strength of concrete after steam curing. Thus, these tests also show that when steam cured concrete is stored under natural conditions in freezing weather at  $-15$ ,  $-20^{\circ}\text{C}$  for 28 days, no significant increase in strength of the concrete occurs.

The strength of concrete increased under natural winter conditions in the studies of M. Yu. Leshchinskiy (Main Administration for Housing and Civil Engineering Construction of the Kiyev Executive Committee). This is due to the fact that the average monthly temperatures in December were  $-3 \dots -7^{\circ}\text{C}$ ; in January  $-5 \dots -9^{\circ}\text{C}$ ; and in February  $-5 \dots -3^{\circ}\text{C}$ .



TABLE 6.13. CHANGE IN STRENGTH OF CONCRETE AT LOW TEMPERATURES UNDER NATURAL CONDITIONS

Rated grade of the concrete	Dimensions of the sample, cm	Humidity upon exposure to freezing weather, %	Compression strength of samples exposed to freezing weather, MPa	Compression strength of thawed samples, MPa, upon exposure to sub-zero temperatures for, days			
				45	75	105	150
300	10×10×10	4,8	27,1	26,2	25,1	24,7	24,8
	10×10×40		19,4	17,9	18	17,3	16,8
500	10×10×10	4,2	51,3	51,5	51,5	51	50,6
	10×10×40		37,4	36,9	36,4	35,4	34,6
700	10×10×10	3,9	57,4	58	58	57	57
	10×10×40		44,7	44,8	43,1	42,8	42

Commas indicate decimal points.

If after hygrothermal treatment the concrete will be under natural conditions at lower sub-zero temperatures, some drop in its strength is even possible. This is confirmed by tests conducted in Eastern Siberia [14]. Concretes of grade 300, 500 and 700 after hygrothermal treatment from 3-5 days were exposed to natural winter conditions in Irkutsk (Table 6.13).

Samples in the form of cubes and prisms were cured outside the facility 150 days beginning in October. During October and the beginning of November the samples underwent cyclical freezing and thawing, and then subjected to the effect of variable sub-zero temperatures which varied 10-20° diurnally. In this case the absolute minimum temperature was -42°C. The data obtained show that as the effect of very low sub-zero temperatures increases the strength of concretes of various grades drops more the less the strength of the concrete and greater its moisture before freezing. Thus, after 150 days of storage under natural freezing conditions the drop in strength of grade 300 concrete was approximately 10%, grades 500-700 almost 5-6%.

The detrimental effect of water saturation of concrete on its strength when exposed to freezing weather was also confirmed by special tests conducted at the Scientific Research Institute of Concrete and Reinforced Concrete. After steam curing some of the samples were placed in a freezing chamber in a dry air state, and some in a water saturated state. The results have shown that in the saturated samples the water in a free state which fills all the open pores and capillaries becomes ice upon freezing and causes large internal stresses which reduce the strength of the concrete. The samples contain considerably less water in dry air and it is found basically in fine pores and capillaries. The water freezes at a lower temperature in these capillaries. Moreover, there are air reserve pores for free expansion of the ice. Consequently, no such structural changes which could reduce the strength of the concrete occur in dry air samples.

Studies conducted by the Scientific Research Institute of Physical-Chemical and Radiometric Measurements on steam cured samples in a high sensitivity dilatometer in a saturated and dry air state have shown that when a water saturated sample is frozen a discontinuity on the dilatometric curve is observed at  $-7, -8^{\circ}\text{C}$  (Figure 6.29), which fixed the transformation of water into ice in the pores and large capillaries, as is a break in the curve at a temperature below  $-30^{\circ}\text{C}$ , which indicates freezing of water in a group of finer capillaries and microcracks. At  $-60^{\circ}\text{C}$  and below, another change in the straight-line of deformations which is associated with freezing of water in the calcium hydrosilicate gels is observed. When the dry air sample was frozen, no discontinuities were observed, and the dimensions of the samples dropped uniformly in accordance with the coefficient of temperature expansion (compression) of concrete. When concrete is frozen at an early age the first discontinuity is recorded not at  $7-8^{\circ}\text{C}$ , but at  $-2 \dots -3^{\circ}\text{C}$  in the dilatometer during the experiment.

It must be noted that the varied humidity state of the steam cured concrete in freezing weather engenders some contradictory data. During different weather water saturation as well as desiccation (in particular sublimation of the ice) of concrete are possible which unconditionally affects the stability of the results in determining strength. It should also be considered that under natural conditions, in contrast to tests in the freezing chamber, the temperature varies considerably over a month. Therefore not only the minimum temperature of any length of time or day, but also the average monthly temperature and its increase during thaws are indicative for evaluating the hardening conditions of the concrete. Thus, the strength of steam cured concrete in freezing weather under natural conditions increases, although slowly, at average monthly temperatures near  $-5^{\circ}\text{C}$  and above.

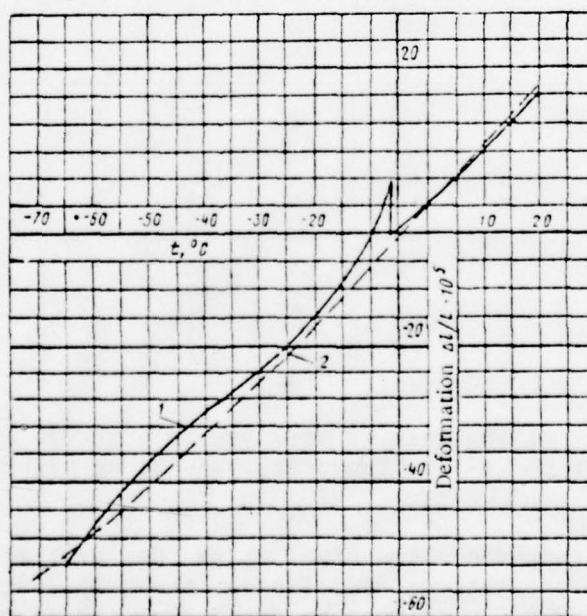


Figure 6.29. Dilatometric Curves of a Steam Cured Concrete Sample. 1, When frozen in a saturated state; 2, The same, in a dry state.

The approximate increase in the strength of steam cured concretes under subsequent hardening conditions and various temperatures is shown in Table 6.14. These generalized data obtained at the Scientific Research Institute of Concrete and Reinforced Concrete may be used to determine the minimum changes in delivery strength of concrete in different climatic zones.

Figure 6.30 shows a generalized curve of the kinetics of the gain in strength by concrete at from 20 to 20°C compiled on the basis of numerous experiments. In this case the hardening of concrete in freezing weather immediately after preparation is intended, i.e., without precuring at an above-zero temperature. As is shown in the figure, some increase in strength at temperatures down to -15°C is observed in light concretes due to the porosity of the aggregates.

TABLE 6.14. APPROXIMATE INCREASE IN THE STRENGTH OF CONCRETE OF GRADES 200-300 CONTAINING PORTLAND CEMENTS AFTER STEAM CURING UNDER VARIOUS CONDITIONS

Concrete strength 12 hrs. after thermal treatment in % of rated strength	Hardening time after thermal treatment, days	Concrete strength in % of rated strength during hardening				
		In a hot humid climate	In a dry hot climate	During warm weather	In a transitional period	In cold weather (-10°C and lower)
50	1	60	60	55	50	50
	3	80	70	65	55	50
	7	95	80	70	60	50
	14	100	80	80	70	50
	28	105	80	100	80	50
70	1	75	75	75	75	70
	3	85	85	85	80	70
	7	105	90	90	80	70
	14	105	95	95	85	70
	28	110	100	105	90	70
85	1	90	95	90	90	85
	3	100	100	95	95	85
	7	110	105	100	95	85
	14	115	105	105	100	85
	28	120	105	115	100	85

The intensity of the gain in strength by concrete in freezing weather after precuring at above-zero temperatures will be higher than shown on the graph.

The graphic representation gives us an idea of the intensity of the hardening of concrete without additives at the temperatures of interest to us, mainly below 0°C. It must be noted that the strengthening of concrete after freezing first begins more intensively than is observed in concrete of the same age which has not been frozen.



The use of alite high aluminate portland cements is recommended in winter concreting. Due to accelerated hydration and heat liberation, these cements ensure the rapid formation of structural strength of concrete and the least losses of it during early freezing.

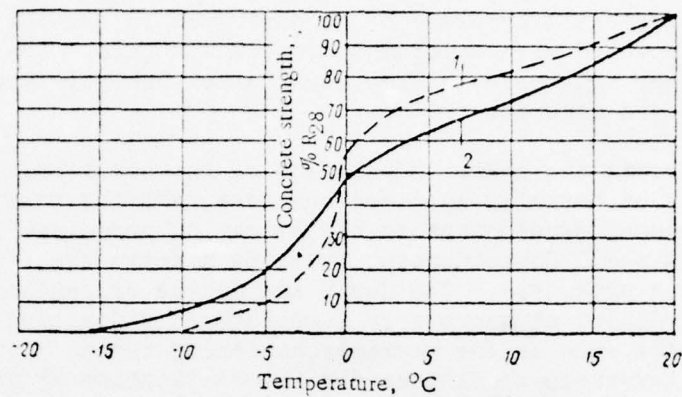


Figure 6.30. Kinetics of the Increase in Strength of Freshly Made Concrete Over 28 Days of Hardening at Temperatures of +20 to -20°C (% of  $R_{28}$ ). 1, Normal concrete; 2, Light concrete.

On the basis of complex experimental studies conducted using modern methods and measuring technique, it is possible to formulate the basic aspects of the hardening of cement and concrete at temperatures below 0°C.

Cement hydration and concrete hardening in freezing weather are directly dependent on the liquid phase content in them which in turn depends on the stage of development of the cement hydration processes before freezing, pore dimensions, cement grinding fineness, the magnitude of the sub-zero temperature and its variation during the curing period. Freezing not only retards, but interrupts the cement hydration processes (partially or completely) and disrupts the physical structure of the cement stone, especially its bonding to the aggregates. The freezing mechanism of cement stone and concrete and the deconsolidation of them occur along the cooling front from the outside into the element.

An increase in the volume of the water becoming ice, beginning with the free water in the macropores, then the capillary water, and at sub-zero temperatures the gel water as well, causes disintegration of the monolithic conglomerate. The earlier freezing occurs, the greater the strength losses, the increase in gas and water permeability and the decrease in frost resistance.

Calculations show that there are sufficient pores in hardened concrete for expansion of the ice, and therefore considerable deformations may occur only when the concrete is completely saturated with water. If necessary, air is artificially entrained in dense concretes for the formation of the optimum number of pores by adding surface active substances. A different picture is obtained when the concrete is frozen at an early age.

Processes which occur in it during freezing and the temperature rise during thawing are extremely complex. For example, a temperature near  $0^{\circ}\text{C}$  (at which hardening occurs) may have a deleterious effect on the formation of the structures, since in this case large crystals of ice form slowly. This phenomenon is especially noticeable in the beginning stage of hardening, when the weak crystalline skeleton is destroyed in the intergrain space which is not packed with calcium hydrosilicate gels. Low temperatures which cause the water to freeze in fine capillaries and gels are more dangerous for hardened concrete.

In frozen concrete the phase composition of the new formations is no different than that of normally hardened concrete, and the possibilities for subsequent development of the hydration processes in the cement are retained. Consequently, freezing affects the kinetics of the cement hydration processes. The depth and degree of cement hydration upon subsequent hardening at above-zero temperatures and adequate humidity may also be quite the same as for normally hardening cement. In the water medium especially favorable conditions for intensification of the cement hydration processes and strengthening of concrete with microstructural dislocations are created after freezing. When concrete or cement stone is frozen at an early age, when they still contain few new formations (at all sub-zero temperatures), dislocations in the macrostructure, and then in the pores and capillaries with radii of from 1000 to 10000 Å are observed. With regard to the gel structure, no dislocations are observed at temperatures down to  $-40^{\circ}\text{C}$ .

These conclusions were drawn on the basis of qualitative and quantitative x-ray analysis, microscopic, including electron microscopic, studies of slides, mercury porometry and on the basis of tests of the water and gas permeability of concrete.

Studies of the mechanism of phase transformations of water and cement hydration have made it possible to explain in a scientific manner the hardening of concrete at sub-zero temperatures. The products of hydration proceeding at sub-zero temperatures are characterized by increased dispersion and adsorbed water content. Later on, effluorescence and consolidation of new formations from the amorphous mass occur. Depending on the intensity of hydration of the cement grains, and the temperature and moisture conditions which cause internal time stresses in the concrete, decreases in strength, but under favorable conditions a further increase in it, are observed. In this case the ordinary processes of hydration hardening continue as the stage of mineral dissolution passes and as the hydrate new formations crystallize out of the supersaturated solutions, with strengthening of the concrete. They proceed slowly with some unevenness when passing through critical temperature points only at low above-zero and sub-zero temperatures.

Some intensification of the hydration processes continues even at temperatures below  $-10 \dots -20^{\circ}\text{C}$  when the cement stone is frozen during the period of brisk hydration which occurs within the limits of attaining 20-50% of  $R_{28}$ , especially after heating. After dense gel shells have formed around the cement grains, the moisture may penetrate within, primarily

by diffusion; the hydration processes slow down in conjunction with this. The low sub-zero temperatures which cause the water to freeze in the pores and fine capillaries exclude this source for a continuation of cement hydration, and consequently concrete hardening in freezing weather. Under similar conditions the concrete is in an anabiotic state. Depending on the ambient temperature, composition and state of freezing of the concrete it exhibits a varied strength in the frozen state.

Concrete in a frozen state should be protected from moisture loss to preserve its ability to gain strength in a normal manner and achieve other physical-mechanical properties later on when favorable temperature-moisture conditions occur. This question was treated previously.

In conclusion, it is interesting to turn to certain points in the development of winter concreting in our examination of the question of concrete hardening at sub-zero temperatures. At the beginning of the thirties, it had already been established that at temperatures below 0°C especially characteristic for fall-spring conditions, concrete gains strength rather intensely.

In conjunction with this, in 1934 in preparing the second edition of "Technical Specifications for Winter Construction", a note was made in the chapter on concrete and reinforced concrete operations in which the author noted that it had been established according to the data of recent studies that in some cases concretes may harden, although slowly, at sub-zero temperatures.

However, at the time there were still not sufficient data to standardize the increase in concrete strength in the technical specifications.

At the present time, instructions for calculating the gain in strength by concretes at sub-zero temperatures are included in standards. The first steps in this direction in the USSR had been made when the delivery strength of concrete in prefabricated articles was established. The hardening of concrete is considered in the handbook on concreting in freezing weather using the "thermos" method for calculations of strength gain and duration of curing. We used the calculation of strength gain in freezing weather quite widely when adding various chemical agents to concrete, especially antifreeze additives which lower the freezing temperature of the liquid phase.

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CHAPTER 7  
THE EFFECT OF EARLY FREEZING ON THE  
INCREASE IN STRENGTH OF CONCRETES  
UPON SUBSEQUENT HARDENING

The effect of early freezing on the properties of concrete has been treated in many works of Soviet scientists: I. A. Kireyenko, B. G. Skramtayev, V. N. Sizov, V. M. Moskvina, V. F. Utenkov, B. A. Krylov, M. M. Kapkin, O. S. Ivanova, as well as foreign scientists: O. Graf, D. Wiley, A. Collins, T. Powers, P. Nerenst, R. Valor, A. Nikenen, H. Scofield et al. These works usually established the effect of freezing of concrete at an early age on the strengthening of it later on during hardening under above-zero temperature conditions. In spite of the great amount of work conducted, there remain many questions which have not yet been explained. Such important questions as the mineralogical and material composition of cements, the type and porosity of the aggregates, the duration of freezing, the magnitudes of the sub-zero temperatures, and subsequent curing of concrete in various media have not been adequately examined. All these and many other researchers have studied, as a rule, the loss in strength of concrete after it is frozen at an early age. However, there is no unified opinion in this question concerning the effect of age for the specific strength achieved before freezing on subsequent hardening of the concrete. The problem of the effect of early freezing on deformative properties, frost resistance, and water and gas permeability of concrete upon subsequent hardening have not yet been studied thoroughly enough.

The studies of Professor I. A. Kireyenko [22, 23] of the effect of early freezing on the properties of a cement paste, mortar and concrete are well known in the USSR. He conducted his first experiment as early as 1910 on concreting operations in freezing weather when building the reinforced concrete girder bridge in Tarashcha. Sudden freezing weather made it necessary to violate the requirements of the technical specifications which prohibited concreting operations at a temperature below  $0^{\circ}\text{C}$ . Concrete placement operations in the girders were conducted using heated water and sand at  $-6^{\circ}\text{C}$ . The form-work was only dismantled in the spring, after which the bridge was examined and tested. A second bridge with a span of 12 m and several smaller reinforced concrete structures were built in 1911.

Having obtained in principle positive results for concreting in freezing weather, I. A. Kireyenko subsequently organized his own initial studies of construction in the laboratory of the Kiyev Polytechnic Institute.

I. A. Kireyenko of the State Construction Institute reported on the effect of freezing weather on concrete at the First All-Union Conference on Concrete and Reinforced Concrete in April of 1930. This report was very timely and engendered great interest among the participants in the conference. Beginning in 1931, he organized studies on winter concreting in the Kiyev Branch of the Ukrainian Construction Institute.

The first publications on the effect of freezing weather on concrete by D. Wiley (U.S.A.) and O. Graf (Germany) had appeared by this time. In 1928, D. Wiley conducted an interesting experiment on the freezing of concrete at ages 0, 1, 3, 5, 7 and 10 days at  $-15^{\circ}\text{C}$  (concrete composition 1:2:3 at a water-cement ratio of 0.8). The cylinders were frozen without forms for 7 days and tested for strength after thawing 1.5-2 hours in a water bath at  $38^{\circ}\text{C}$ .

On the basis of these tests, D. Wiley drew the conclusion of the so-called "critical age" and requirements for curing concrete before freezing (Figure 7.1). In these tests the concrete mixture was prepared with a high W/C (0.8) and the samples were cured in a cooling chamber without forms. Therefore freezing caused a deficit in the concrete strength up to age 7 days. These tests were repeated by I. A. Kireyenko, V. M. Moskvina and ourselves. For a long time the question of critical age or more correctly of critical strength of concrete before freezing was the subject of discussion. O. Graf also conducted experiments on the freezing of concrete at an early age. In this case the effect of repeated freezing on the properties of concrete was studied. He concluded that concrete exposed to a small number of freezing and thawing cycles without water saturation should have a strength of at least 8 MPa before the first freezing, and at least 15 MPa upon repeated freezing and thawing in water. O. Vellmi (Switzerland) shared this same point of view.

Later works also expressed different points of view which do not adequately match the requirements of practice, and as a rule, do not meet the official requirements of the technical specifications.

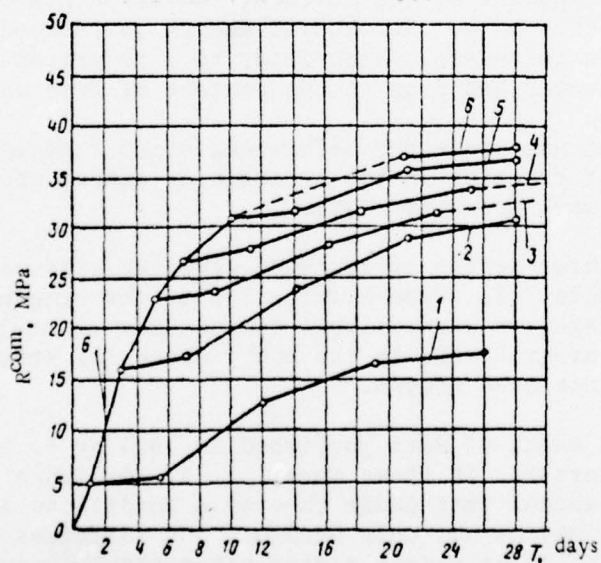


Figure 7.1. Effect of a Sub-Zero Temperature on the Strength of Concrete (According to D. Wiley). 1, 24 hours freezing; 2, 3 days freezing; 3, 5 days freezing; 4, 7 days freezing; 5, 10 days freezing; 6, Without freezing.

H. Scofield (U.S.A.) believes that the time of preliminary hardening before freezing varies from within 12 to 60 hours, depending on the W/C. M. Niss (FRG) believes 12 hours to be adequate for curing of concrete before freezing at a W/C = 0.6. The critical strength of concrete varies greatly according to the data of different researchers (from 2.5 to 15 MPa). To a certain degree this may be due to the quality of the cements and aggregates used, the climatic conditions of different countries, as well as to the abstracting of laboratory data from practice. However, as P. Nerenst noted in his report at the Fourth International Congress on Cement Chemistry, "this question still requires further study and in the meantime it is not possible to draw any final conclusions with regard to the time at which macroscopic segregation of ice is prevented by the progressing process of hardening" [45].

In conjunction with a revision of certain aspects of SNip III-V.1-62, we conducted special tests to determine the "critical strength" in the laboratory of the Scientific Research Institute of Concrete and Reinforced Concrete in 1964-1966. The results of these tests are cited later.

#### Increase in the Strength of Cement Stone and Mortar After Freezing at an Early Age.

Samples of cement paste and cement mortar of various compositions were first tested to determine the effect of premature freezing on change in structure and increase in strength in time. For these reasons different chemical and finely ground substances were added to the cement paste and mortars. As structural studies have shown, finer ice crystals form when salts are added due to gradual freezing and to the drop in the freezing point of the saline component of the mixture; the structure of the samples is less disrupted in this case. Structural damage is reduced as the density of the samples increases, which leads to a reduction in the number of pores filled with water and drop in the content of free water.

The strength test was conducted before and after freezing the samples to trace the effect of freezing on the strength of cement stone and mortar. Some results of this work are cited later.

The results of three series of tests on freezing samples of cement paste are shown in Table 7.1. Upon examination of the cement stone after freezing at an early age, it was possible to see that channels had formed which disrupted its integrity and in the end reduced its strength compared to samples which had not been frozen.

The results of a check of data published in 1934 by I. A. Kireyenko are of undeniable interest. In these works, I. A. Kireyenko showed and it was confirmed by the author that under favorable conditions early freezing of wet cement mortars may be not only harmful, but sometimes useful. The compression strength of a wet cement mortar after thawing may not decrease, but conversely, increase. The strength of compacted mortars after freezing drops as a rule. As the freezing times of the mortars lengthen, the losses in their strength, as in concretes, drop later on.



TABLE 7.1. LOSSES OF STRENGTH BY SAMPLES OF CEMENT PASTE OF NORMAL THICKNESS AFTER FREEZING AT AN EARLY AGE AND HARDENING 28 DAYS UNDER NORMAL CONDITIONS

Hardening conditions	First series of samples		Second series of samples		Third series of samples	
	28 day strength, MPa	Strength losses, %	28 day strength, MPa	Strength losses, %	28 day strength, MPa	Strength losses, %
Normal storage	60	—	71.8	—	60	—
Frozen immed. after preparation	41.6	30.7	49.7	30	41.3	30
Frozen 4 hrs. after prepar.	39.2	34.7	—	—	39.2	35
Frozen 9 hrs. after prepar.	—	—	55	23.4	—	—
Frozen 12 hrs. after prepar.	53	20	58	19	52	13
Frozen 24 hrs. after prepar.	63.1	No losses	64.3	9	60.1	No losses
Frozen 72 hrs. after prepar.	—	—	—	No losses	—	—

Commas indicate decimal points.

The results of tests using the freezing of a wet mortar containing grade 300 portland cement are cited to confirm what has been said. The composition of the mortar by volume depending on the W/C varied from 1:2.74 to 1:4.55. At first the series of samples at age 2 hours 30 minutes after preparation were frozen 3 days at  $-15 \dots -20^{\circ}\text{C}$ . After this period in the freezing unit the samples were placed under normal conditions for 7 and 28 days together with control samples (at  $17^{\circ}\text{C}$  and 95% air humidity).

The test and control samples were compression tested after 7 and 28 days of normal storage. The results of the tests of mortar strength are cited in Figure 7.2.

In all cases the strength of the frozen mortar was higher than the strength of the mortar stored under normal conditions for the entire period. The greatest increase in strength (approximately 200%) was observed when the water-cement ratio of the mortar was increased.

The second series of tests was conducted with a mortar at a W/C = 0.83 containing the same portland cement. The samples were frozen immediately after preparation, after 6 hours, after 1 and 5 days. As can be seen in Figure 7.3, in this case the samples frozen soon after preparation acquired

greater strength after normal storage than control samples. Samples frozen at age 1 and 5 days exhibited a drop in strength compared to control samples after 28 days of normal hardening.

As other tests have shown, not all cements and not all placement and thawing conditions for a mortar result in an increase in the strength of a mortar frozen soon after its preparation. The strength increases more rarely than it decreases. The results depend to a great extent on air entrapment, water content, the sample freezing rate.

After verifying tests were conducted and separate positive results obtained on the freezing of cement mortars, in 1935 we began to study the effect of sub-zero temperatures on the strength of lime-cement (mixed) mortars. This was necessary because the refrigeration method of laying brick introduced at the time was used most often for compound mortars, and problems of mortar technology during winter concreting had not yet been theoretically developed. The results of research made it possible to evaluate and confirm the method of refrigerating masonry which had been promoted by use.

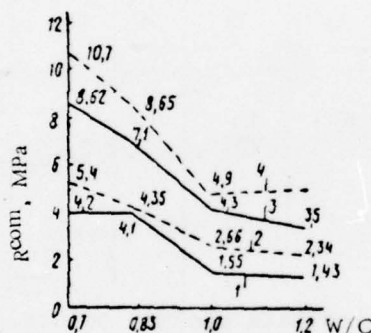


Figure 7.2. Strength of a Wet [Plastic] Mortar Frozen 2 Hours 30 Minutes After Preparation and Hardened 7 and 28 Days Under Normal Conditions. 1, 7 days storage under normal conditions; 2, 3 days freezing, then 7 days storage under normal conditions; 3, 28 days storage under normal conditions; 4, 3 days freezing, then 28 days storage under normal conditions.

Tests were conducted using grade 400 portland cement from the Novo-rossiyskiy Factory and grade 200 slag portland cement from the Kosogorskiy Factory. The mortar was used at a composition of 1:2:10 by volume (cement:lime paste:sand or slag) in compacted and in plastic samples. Test samples  $7 \times 7 \times 7$  cm in wooden forms were placed in a cooling chamber at a temperature which varied within from  $-14$  to  $-20^{\circ}\text{C}$ . Freezing of the mortar began immediately, 3, 12 and 24 hours after preparation of the samples. Some of the samples remained in the freezing unit 3 days, and some 28 days to ascertain the import of the length of freezing. After completion of freezing, test samples were stored 7, 28 and 56 days under normal conditions.

Figure 7.4 shows the results of strength tests of compacted mortar after having been frozen for 28 days.

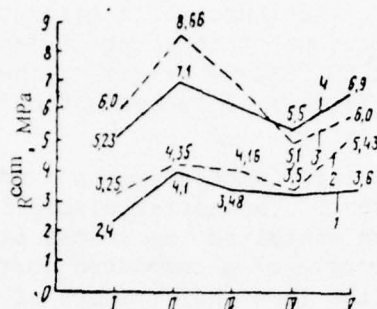


Figure 7.3. Strength of a Wet Cement Mortar After 3 Days Freezing at Different Ages and Subsequent 7 and 28 Days Storage Under Normal Conditions. 1, 7 days storage under normal conditions; 2, 3 days freezing, then 7 days storage under normal conditions; 3, 3 days freezing, then 28 days storage under normal conditions; 4, 28 days storage under normal conditions.

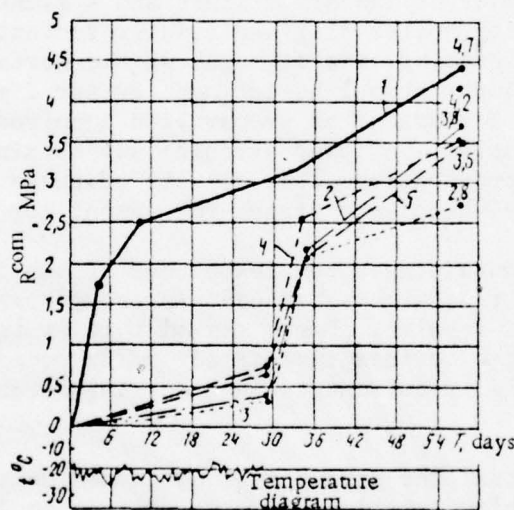


Figure 7.4. Increase in the Strength of a Mortar of Composition 1:2:10 in Compacted Samples After 28 Days Under Freezing Conditions. 1, Normal storage conditions; 2, Frozen immediately after preparation; 3, Frozen 3 hours; 4, The same, 12 hours; 5, The same, 24 hours.

In all cases of storage of samples under normal conditions, the strength of the mortar increased rather intensively after it was frozen. In this case superior results were obtained at 28 days curing under freezing conditions. After 7 and 28 days of normal storage following 28 days freezing the strength of the mortar reaches 100% of the strength of its control samples. Somewhat poorer results were obtained in mortar exposed to freezing conditions 3 hours after placement.



In a lightweight mortar, the increase in strength after 3 days under freezing conditions is more intense than after 28 days. In a compacted lightweight mortar subjected to 28 days freezing, the strength losses reached 19-35% of  $R_{28}$  after 28 days of subsequent normal storage.

Practically the same picture is observed in a compacted mortar containing slag portland cement. The mortar placed in the freezing unit immediately after preparation exhibited the lowest strength after freezing and normal storage. The strength of a compacted mortar exposed to early freezing is 10-20% less in time than the strength of a mortar hardened under normal conditions for the entire period. In this case the actual grade of the mortar is achieved upon freezing in all cases in due time.

A different picture is obtained when freezing a plastic mortar. Compacting of the mortar exceeds the compression of the mortar in the masonry seam, therefore the conditions for consolidating the mortar in the masonry seam will be of intermediate value. Figure 7.5 shows the results of strength tests of a plastic mortar after freezing for 3 days.

One series of samples was prepared from a mortar of sand and a water content of 17% of the mass of the dry mixture and a slump of 2.5 cm, the second from a mortar with boiler slag and a water content of 31.2% and slump of 2 cm. After freezing, the strength of the mortar increased intensively upon subsequent normal hardening. By age 2 months, the samples frozen immediately and 3 hours after preparation acquired a strength above that of the control samples. A lower strength was obtained in samples frozen 24 hours after preparation. The results of these studies coincide on the whole with those which were stated for cement mortars.

Plastic mortars containing a complex binder at sub-zero temperatures for a longer period of time with subsequent spring temperatures do not yield substantially different results. Tests showed that it is more advantageous to freeze plastic mortars immediately after preparation. This coincides with industrial requirements when working according to the masonry refrigeration method.

It must be noted that the strength of compacted mortars (in spite of the loss in strength which sometimes reaches 40%) is no lower in terms of absolute values than that of plastic mortars. Tests conducted in 1934 in the study of the cohesion of mortar to brick have demonstrated a certain advantage of plastic mortars over compacted ones. Therefore in due time the "trowel" method of winter bricklaying (with a thick mortar) was replaced by "injection" bricklaying in the technical specifications. This made it possible to increase the productivity of bricklayers, reduce the settling of walls and improve the quality of masonry erected using the refrigeration method.

In 1939, A. L. Volovsyatskiy published the data from his tests at the Southern Scientific Research Institute of Industrial Construction in which he stated that in freezing weather cement mortars with a low W/C harden intensively. In conjunction with this, the author considered it necessary to conduct verifying tests. For this reason, samples of mortar of composition 1:3 containing grade 300 portland cement at a W/C = 0.25; 0.35; 0.45; 0.55 were prepared.

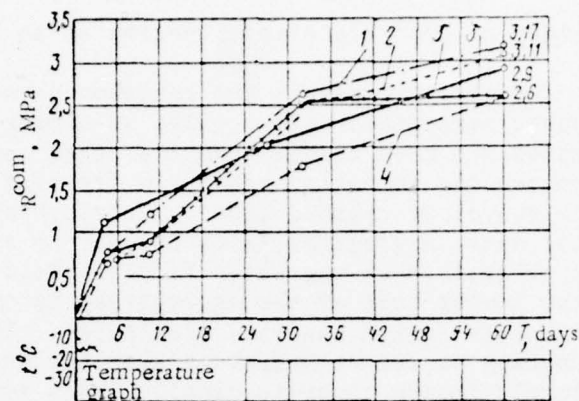


Figure 7.5. Increase in the Strength of a Plastic Mortar of Composition 1:2:10 After 3 Days Under Freezing Conditions (Slag Sand is Used as the Aggregate). 1, Frozen immediately after preparation; 2, Frozen after 3 hours; 3, The same, after 12 hours; 4, After 24 hours; 5, Normal storage conditions.

In the first 3 cases the mortar was compacted on a standard ram impact machine, and in the last case it was placed with vibration. Samples prepared under normal conditions were placed in a cooling chamber after 1 hour in which the temperature varied from  $-8$  to  $-21^{\circ}\text{C}$  over 24 hours. At age 7 days the normally stored samples and the frozen samples were compression tested. The results of the tests on the mortar after exposure to freezing conditions for 7 days are shown in Table 7.2.

TABLE 7.2. MORTAR STRENGTH AFTER EXPOSURE TO FREEZING CONDITIONS

W/C	Compression strength, MPa			
	Immediately after freezing	1 hr. after thawing	24 hrs. after thawing	7 days of normal storage
0.25	5.54	Destroyed	1.55	7.2
0.35	8.14	0.25	2.24	12.5
0.45	12.8	0.76	—	13.1
0.55	14	0.8	—	11.7

Commas indicate decimal points.

It can be seen from the data that the mortar with a  $W/C = 0.25$  subjected to freezing has no strength upon complete thawing. Samples of mortar with a greater content of frozen water did not thaw at all in 1 hour (the core of the cubes remained frozen upon testing), and therefore the sample exhibited a strength of 0.3-0.8 MPa after testing. After 24 hours of normal storage following 7 days of freezing, the mortar still acquired some strength. In a frozen state the strength of the mortar was greater the greater the water-cement ratio. The maximum strength in the frozen state reached 14 MPa. Thus, the test showed that the statements which had been made were the result of a faulty test procedure. The mortar was clearly tested in a frozen state, with which the author of the proposition would have had to agree.

### Increase in the Strength of Concrete After Freezing at an Early Age.

Early freezing of concrete disrupts the cohesion between the mortar and grains of the coarse aggregates. As a rule, at winter construction sites, coarse aggregates are used colder than the other components of a concrete; this promotes the formation and rapid freezing of a water layer on the surface of the gravel or crushed stone. Poor cohesion of the coarse and, in particular the dense aggregates, with the mortar as the result of the formation of ice crystals when the water film on their surface freezes (principally under the lowest part of the aggregates) is observed when testing and demolishing prematurely frozen concrete structures. Therefore, in spite of the resumption of cement hydration with the onset of above-zero temperatures, prematurely frozen concrete usually loses some of its ultimate strength later on.

The strength losses of concrete are greater the earlier it has been frozen. The effect of early freezing on the properties of concretes has been studied using various cements and the most varied freezing and thawing conditions. A great deal of work was done with the participation of Ye. Ye. Dornbush and G. F. Shtal in 1934-1938 on concrete containing different cements in a freezing chamber. The test concrete samples were frozen at various ages after preparation. At first the tests were conducted with concrete containing portland cement, later on tests were conducted on concrete containing slag portland cement, pozzuolanic portland cement, and finally bauxite cement in accordance with the procedure adopted.

A test to examine the question of the amount of increase in concrete strength during the cooling process of the samples in freezing weather and upon thawing them in the laboratory before the test were conducted first. Cubes  $20 \times 20 \times 20$  cm prepared in metal forms were used as the test samples. The concrete had a composition of 1:2:3.9 (by volume) at a W/C = 0.69 and a slump of 10 cm. The samples prepared were cured 24 hours in the building at  $14^{\circ}\text{C}$ , then placed in a cooling chamber at  $-20^{\circ}\text{C}$  where they remained for 3 days. The samples were tested after 1 and 4 days of normal storage. Some samples were tested when they had cooled down to  $3^{\circ}\text{C}$ , others after freezing and thawing up to  $4^{\circ}\text{C}$ . Samples were again tested after completing 3 days of freezing and 1 day in the building at  $15^{\circ}\text{C}$ .

As can be seen from Figure 7.6, no increase in strength occurred during the 3 days the concrete was in a frozen state. A small increase in strength occurred during the cooling and thawing process of the samples, especially when the samples were in the building for entire days. In the latter case the strength with 0.5 MPa at age 24 hours increased up to 1.3 MPa.

The kinetics of freezing and thawing of samples  $10 \times 10 \times 10$  cm at  $-5$ ,  $-10$  and  $-20^{\circ}\text{C}$  is shown in Figure 7.7. As can be seen from the graph, the temperature in the core of the sample drops rather rapidly to  $0^{\circ}\text{C}$  (during 1-2 hours). At a temperature near  $1^{\circ}\text{C}$ , horizontal plateaus which characterize the transition of the liquid phase into ice which is accompanied by the liberation of heat are observed on the graph; in conjunction with this the temperature of the sample remains constant for some time. In this



case, the lower the temperature below zero at which freezing occurs and the smaller the sample, the smaller these plateaus.

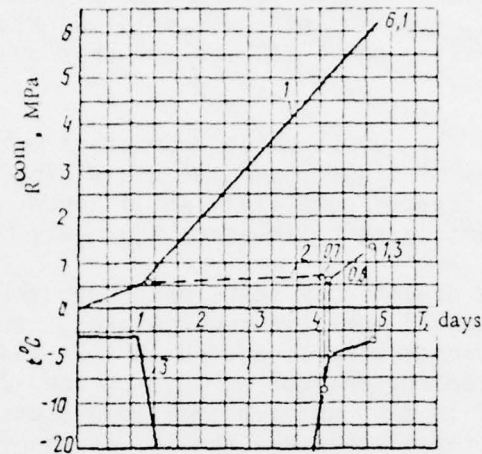


Figure 7.6. Increase in the Strength of Concrete in the Freezing and Thawing Period. 1, Under normal storage conditions; 2, When frozen; 3, Temperature in the frozen cubes.

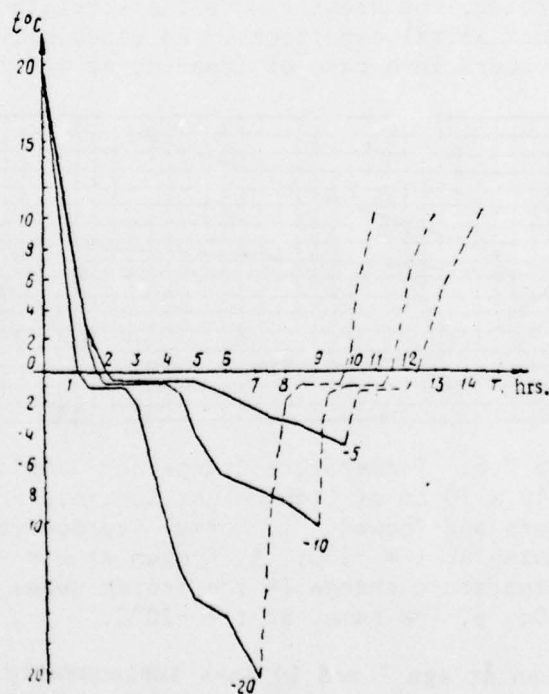


Figure 7.7. Characteristics of the Freezing and Thawing Temperature of Concrete Samples  $10 \times 10 \times 10$  cm at  $-5$ ,  $-10$  and  $-20^{\circ}\text{C}$ . —, Freezing; ----, Thawing.

In our case it took almost 7 hours at  $-20^{\circ}\text{C}$  for the sample to reach the temperature of the chamber, at  $-10^{\circ}\text{C}$  almost 9 hours, and at  $-5^{\circ}\text{C}$  10 hours. The same can be stated about the time of its thawing. At temperatures from  $-1$  to  $-2^{\circ}\text{C}$ , freezing of the sample was slower than at  $-5^{\circ}\text{C}$ , due to which there are greater possibilities for this concrete to gain strength [3].

Figure 7.8 shows the curves which characterize the kinetics of cooling and thawing of samples of light concretes containing volcanic slags. At  $-20^{\circ}\text{C}$  light concrete freezes completely in 11 hours, whereas it is 7 hours in normal concrete containing a limestone aggregate (Figure 7.7).

After conducting preliminary tests and thoroughly studying the procedure of the action of sub-zero temperatures, studies with concretes containing various cements were conducted in 1934-1940. Samples  $20 \times 20 \times 20$  cm were frozen in a cooling chamber at  $-5$ ,  $-10$  and  $-20^{\circ}\text{C}$ . The samples were stored 0, 1, 3, 7 and 10 days under normal conditions before freezing. It must be noted that after placing the samples in the freezing chambers the temperature in them increased to  $0^{\circ}\text{C}$ , and then gradually dropped to  $-5$ ,  $-10$ ,  $-20^{\circ}\text{C}$ .

The results of strength tests of concrete when freezing samples at  $-5$  and  $-20^{\circ}\text{C}$  are shown in Figures 7.9 and 7.10. These data were obtained by testing concrete samples 24 hours after removing them from the cooling chamber. As can be seen from the figures, in both cases the earlier the concrete was frozen, the greater were the strength losses upon subsequent hardening under normal conditions. An especially great lag in the strength increase occurs in a case of freezing at age 1 day.

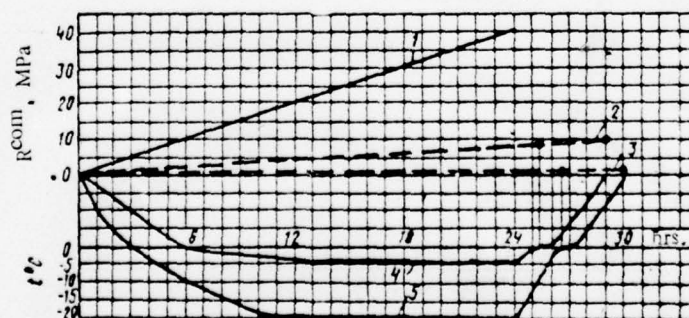


Figure 7.8. Temperature Change for Samples  $10 \times 10 \times 10$  cm of Lightweight Concrete Frozen 24 Hours and Thawed: 1, Normal storage conditions; 2, Frozen at  $t = -5^{\circ}\text{C}$ ; 3, Frozen at  $t = -20^{\circ}\text{C}$ ; 4, Temperature change in the frozen cubes at  $t = -5^{\circ}\text{C}$ ; 5, The same, at  $t = -20^{\circ}\text{C}$ .

Concrete frozen at age 7 and 10 days subsequently acquires a strength practically equal to that of normally hardened concrete. The increase in the strength of concrete which is obtained after 7 and 28 days in a frozen state should be attributed primarily to the slow cooling of the samples and subsequent 24 hour thawing before testing on a press. After the concrete has been

exposed to freezing conditions for 28 days the strength losses were greater than after 7 days. They reached 26% after one month of hardening under normal conditions.

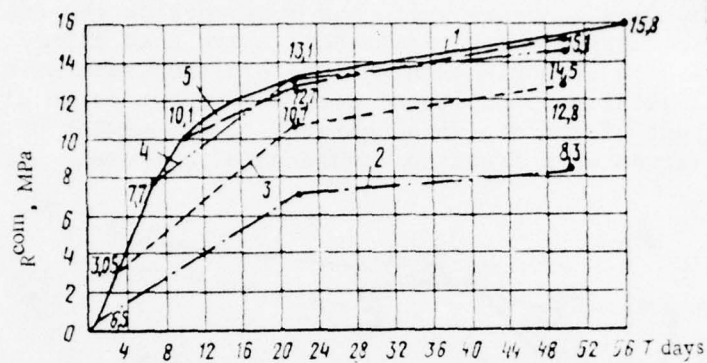


Figure 7.9. Effect of Freezing at  $-5^{\circ}\text{C}$  For 7 Days on the Subsequent Increase in Strength of Concrete Containing Portland Cement. 1, Normal storage conditions; 2, Frozen 1 day; 3, Frozen 3 days; 4, Frozen 7 days; 5, Frozen 10 days.

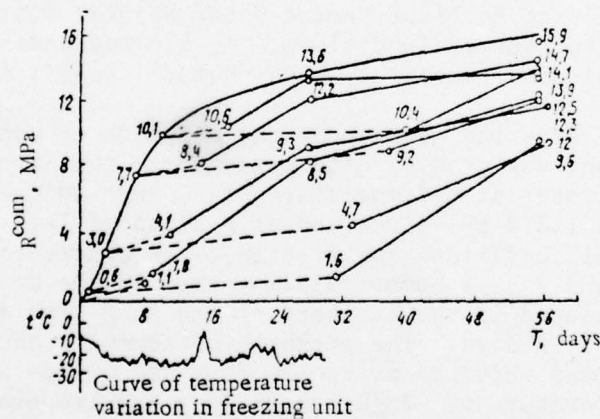


Figure 7.10. Effect of Freezing at  $t = -20^{\circ}\text{C}$  on the Subsequent Increase in the Strength of Concrete Containing Portland Cement (the Dotted Line Shows Samples Exposed to Freezing Conditions for 7 and 28 Days).

Figure 7.11 shows the results of tests on the freezing of concrete containing Novorossiyskiy grade 400 portland cement under natural conditions. Samples exposed to freezing weather 4 hours after preparation remained under winter and spring temperature conditions for subsequent hardening. As can be seen from the figure, the strength losses of concrete outside from the beginning of February and during the entire summer were



small. The mixture was also placed in wooden forms  $20 \times 20 \times 20$  cm; the concrete composition was 1:1.8:3.6 (by volume) at a W/C = 0.65 and a slump of 17 cm.

At age 180 days concrete which had been outside the entire time beginning in February acquired a strength above that rated. The rather intense increase in strength at high sub-zero temperatures may be explained by the mineralogical composition of portland cement (high alite with an increased content of tricalcium aluminate). In a number of cases a similar picture is observed when freezing concretes of extremely workable mixtures.

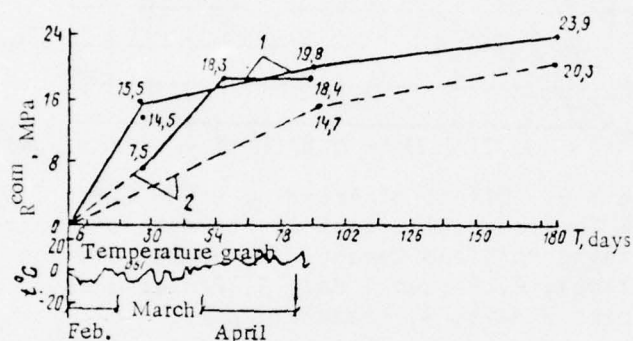


Figure 7.11. Increase in Strength of Concrete Containing Portland Cement Under Natural Winter, and Then Summer Conditions. 1, Storage under normal conditions; 2, Under natural conditions.

The effect of freezing weather on the strength of concrete containing slag portland cement was studied with cement from the Kosogorskiy Factory. The samples were frozen at a temperature of  $-5$  and  $-20^{\circ}\text{C}$  with a concrete composition of 1:2.1:3.8 by volume and at a slump of 7-10 cm. To create perfectly identical conditions for freezing, the concrete samples were prepared 7, 3, 1 and 0 days before placing them in the cooling cabinet. The samples were placed in the cabinets at the same time and cured at  $-5$  and  $-20^{\circ}\text{C}$  for 3 and 28 days. The strength of normally hardened concrete equal to 11.6 MPa was obtained at age 30 days and by age 56 days 13.6 MPa. At an average temperature of  $-20^{\circ}\text{C}$  for 28 days the temperature in the cooling cabinets in the tests varied within from  $-12$  (at the moment the samples were placed in them) to  $-25^{\circ}\text{C}$ . The temperature increased to  $0^{\circ}\text{C}$  during the first hours after pouring the concrete and placing the samples in the cooling chamber, and it then quickly dropped to that prescribed. The results of tests on entire series of test samples are shown in Figure 7.12 which shows that the curves of the increase in the strength of concrete after freezing are below the curves of the increase in strength of normally hardened concrete.

A general picture of the increase in strength was the same as after freezing at  $-5^{\circ}\text{C}$ . The earlier the samples were frozen, the greater were their strength losses. Only it should be noted that at  $-20^{\circ}\text{C}$  there is no increase in strength for the period the samples are exposed to freezing

conditions. At  $-5^{\circ}\text{C}$  for 28 days a clear increase in the strength of concrete containing slag portland cement is noted. Therefore we may conclude that some intensification of the cement hydration reaction occurs in freezing weather, when not all the water freezes in the capillaries. This is especially noticeable after freezing the concrete not immediately after preparation, but after 3 and 7 hours of normal hardening. An increase in strength at  $-20^{\circ}\text{C}$  as well was noted in their twins.

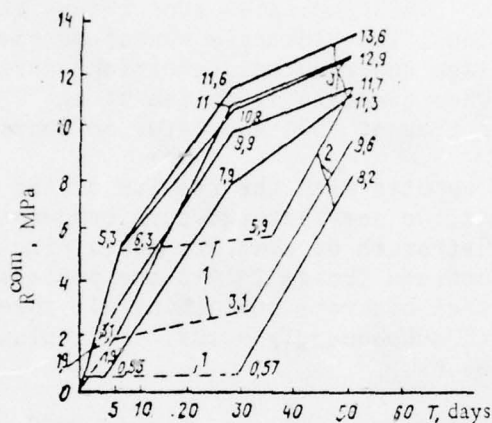


Figure 7.12. Effect of Freezing at  $t = -20^{\circ}\text{C}$  on the Hardening of Concrete Containing Slag Portland Cement. 1, Hardening in freezing weather; 2, The same, under normal conditions; 3, Control samples.

Freezing of the concrete at a lower temperature did not increase the strength loss later on. On the whole, we must conclude that sub-zero temperatures have an identical effect on concrete containing portland cement as well as that containing slag portland cement. The crux of the matter lies in the strength which the concrete acquires at the instant it freezes. It has been noted more than once that slag portland cements are damaged even less by the action of low temperatures. The latter is apparently due to the low water retention ability of this cement which ensures dense concrete placement.

The effect of early freezing on the hardening of concrete containing pozzuolanic portland cement was studied to the same degree as that containing slag portland cement in 1934. Cement delivered from the Bryanskiy Factory was of grade 250. The concrete was used at a composition of 1:2:3.9 by volume of a workable mixture at a  $W/C = 0.69$  and cement consumption of  $270 \text{ kg/m}^3$ . Test samples  $20 \times 20 \times 20 \text{ cm}$  were frozen at  $-5$  and  $-20^{\circ}\text{C}$  for 8 and 29 days. The samples were placed in the cooling chambers and cabinets at age 0, 1, 3 and 7 days after preparation. After the samples were cured for the prescribed periods under freezing conditions, they were stored under normal conditions and tested at age 10, 31 and 56 days. The concrete samples were exposed to freezing conditions at the same time (by series) for which concreting was conducted 7, 3, 1 and 0 days before the beginning of freezing.

The results of the tests have shown that concrete containing pozzuolanic portland cement does not harden at all when frozen in freshly made forms at  $-5^{\circ}\text{C}$ . Nor did concrete frozen at age 1 day and cured for the period assumed yield an increase in strength. After 23 days of storage under normal conditions following 8 days freezing, this concrete acquired approximately 68% of the strength of concrete hardened for the same period under normal conditions. In concrete frozen at age 3 days after curing at  $-5^{\circ}\text{C}$  for 8 and 29 days and cured 1 day under normal conditions before the test, the strength increased 1.8 and 1.6 MPa. This indicates some intensification of the concrete hardening reaction. This increase cannot be completely attributed to the single day of storage under normal conditions during the thawing period of the samples. When concrete is frozen at age 7 days the strength clearly increases for the time at  $-5^{\circ}\text{C}$  and later on increases even more.

If we compare these results with the results of the tests of concrete containing portland cement, we see that sub-zero temperatures are largely reflected in the drop in strength of concrete containing pozzuolanic portland cement. At  $-20^{\circ}\text{C}$  concrete frozen in all the periods, except for 7 days, does not harden. When concrete containing all three cements is frozen, losses in strength subsequently occur. Pozzuolanic portland cement exhibited the greatest losses.

Two tests using the same procedure at  $-5$  and  $-20^{\circ}\text{C}$  were conducted in 1936 to establish the degree of the effect of sub-zero temperatures on the strength of concrete containing bauxite cement. The cement used was from the Amvroziyevskiy Factory which was manufactured using the clinkering method, concrete composition 1:2.5:4 by volume at a  $\text{W/C} = 0.75$  with a slump of 9 cm. No large deviations in temperature were observed in the cooling chambers during the tests.

The concrete was exposed to freezing conditions at age 0, 1 and 3 days. Samples frozen at age 1 and 3 days were prepared beforehand to ensure identical and simultaneous freezing. By the end of 3 and 28 days of freezing the samples were tested after normal storage for 1, 28 and 62 days, i.e., after curing at an age of up to 90 days. The results of analysis of one of the tests are shown in Figure 7.13.

The results were considerably different from those observed in similar studies of concretes containing portland, pozzuolanic and slag portland cements. Early freezing is little reflected in the final strength of concrete containing bauxite cement.

Freezing at  $-20^{\circ}\text{C}$  more quickly interrupts hardening and later on yields a somewhat poorer result than at  $-5^{\circ}\text{C}$ . In the latter case the concrete acquires some strength before the liquid phase freezes. In all cases by 60 days the strength of concrete samples reaches the strength of control samples of the same age, with a few exceptions. In the test at  $-5^{\circ}\text{C}$  when the strength of the control samples by age 57 days was 23.7 MPa, only the samples frozen immediately for 28 days exhibited a strength of 20.3 MPa, i.e., 14% less than the control samples, and in the remaining cases the deviations did not exceed 0.5-0.6 MPa, i.e., they were within the limits of accuracy of the tests. In the test at  $t = -20^{\circ}\text{C}$  by 56 days at which



the duration of freezing plays a lesser role, with the strength of the normally hardening concrete 25.6 MPa, a lower strength was obtained as well in the case of freezing immediately for 28 days - 22.6 MPa, i.e., 10% lower than the normal strength. Concrete frozen at age 1 day exhibited a strength of 10.8-15 MPa when tested after 24 hours of thawing, and that frozen at age 3 days 19.5-20.3 MPa.

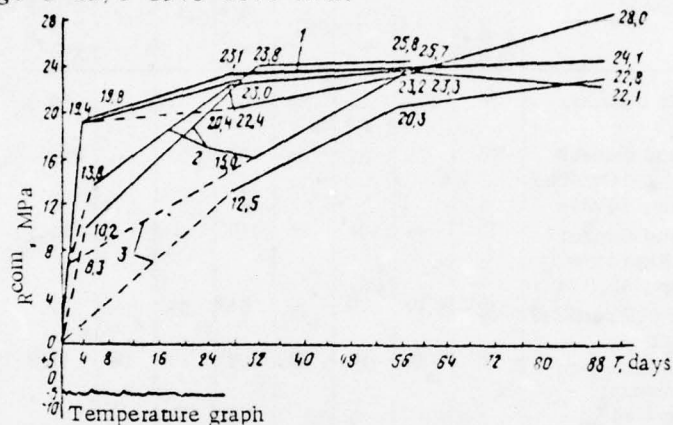


Figure 7.13. Effect of Freezing at  $t = -5^{\circ}\text{C}$  on the Hardening of Concrete Containing Bauxite Cement. 1, Compression strength of control sample; 2, Compression strength of samples stored under normal conditions after freezing; 3, Compression strength of frozen samples.

We may conclude that sub-zero temperatures have almost no deleterious effect on the final strength of concrete containing bauxite cement which has been calcined in a revolving furnace. Some difference was obtained in tests in 1938 in which grade 400 fused bauxite cement was used. The concrete composition was 1:3:4.4 (by volume),  $W/C = 0.78$ , cement consumption  $230 \text{ kg/m}^3$ . The concrete was frozen at age 0.5; 1 and 2 days. An increase in the curing time of the samples before the beginning of freezing did not improve the results. Subsequently the strength was near the strength of normally hardened samples in all cases.

In 1939 we studied the increase in strength of concrete containing various cements after freezing at an early age in the Central Laboratory of Construction Concretes of the Kuybyshevskiy water engineering system. The concrete contained six different cements. Table 7.3 shows the principal data on the cements and the results of tests.

Average quality sand and gravel were taken from the Dmitrovskiy Quarry. Cubes  $20 \times 20 \times 20 \text{ cm}$  were used as the test samples. The concrete mixture placed in metal forms with the aid of vibration exhibited a slump of 3-5 cm. All test conditions and materials were completely identical. The concrete samples were taken from the normal storage chamber and placed in the cooling chamber at age 0, 1, 2, 3, 5, 7 and 15 days. The average temperature in the cooling chamber was maintained at  $-20^{\circ}\text{C}$  for 5 days. After freezing the concrete samples were again placed in the normal storage chamber in which the temperature was maintained at  $18^{\circ}\text{C}$  at maximum air humidity.

TABLE 7.3. EFFECT OF 5 DAY FREEZING AND 30 DAY NORMAL HARDENING ON CONCRETE STRENGTH

Cement	Immed. after placement	Sample strength, % of $R_{30}$ , at age, days						Strength after 30 days of normal harden- ing, MPa
		1	2	3	5	7	15	
Bauxite cement, 50 MPa	70	102	103	99	—	—	—	49.5
Portland cement from "Red October" Factory, 46 MPa	70	71	82	84	90	91	—	31
Portland cement from Kramatorskiy Factory, 42.3 MPa	73	99	104	95	110	—	—	24.9
Grade 300 portland cement	60	80	79	88	94	94	—	21
Pozzuolanic port- land cement, 196 kg + 84 kg tripoli (containing cement from "Red October" Factory.	60	88	96	99	108	86	95	18.3

Commas indicate decimal points.

The 5 day freezing period was not considered in processing the results when calculating the age of the concrete. Normally hardened control samples were tested at age 1, 2, 3, 5, 7 and 15, 30, 180 days. The samples subjected to freezing were tested after the expiration of the overall 30 and 180 days of normal storage.

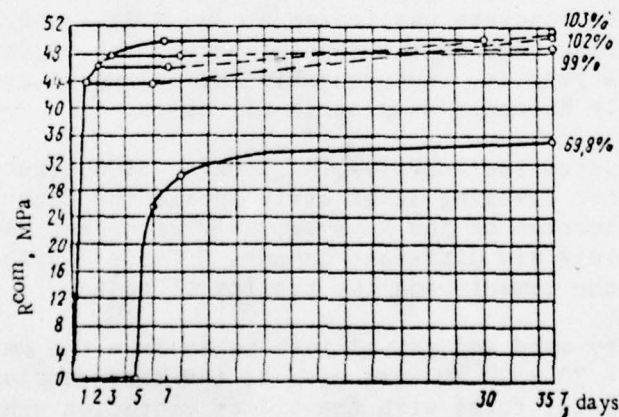


Figure 7.14. Effect of Freezing at  $t = -20^{\circ}\text{C}$  at an Early Age on Subsequent Hardening of Concrete Containing Bauxite Cement.

Thus, it was possible to trace the hardening of concrete after freezing for 6 months. This test enables us to make a judgment about the amounts of the increase in strength for a similar summer period after the concrete had once been prematurely frozen in winter. The results of the tests of concrete strength after 5 day freezing at an early age and 30 days of subsequent normal hardening are shown in Table 7.4 and in Figures 7.14-7.20 for a series of tests.

In these figures the concrete strength is plotted in terms of absolute values in MPa, and the final strength after 30 days of normal hardening is shown in percentages of  $R_{30}$ . The dotted line on the figure shows the hardening of concrete under normal conditions. Tests have shown that the greatest percent of strength loss in the concrete is obtained in those cases in which freezing begins soon after its preparation.

The losses in strength are as a rule less the later the concrete is frozen.

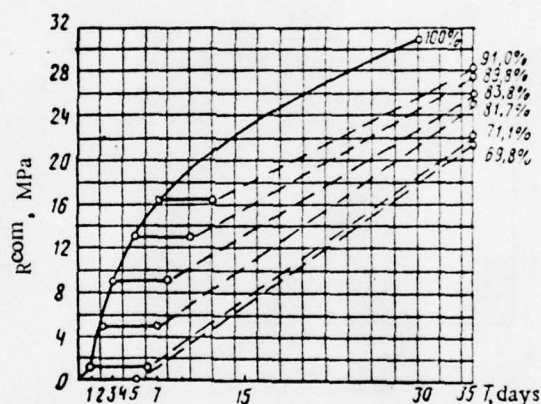


Figure 7.15. Effect of Freezing of Concrete Containing Grade 400 Portland Cement at an Early Age on Subsequent Hardening Under Normal Conditions.

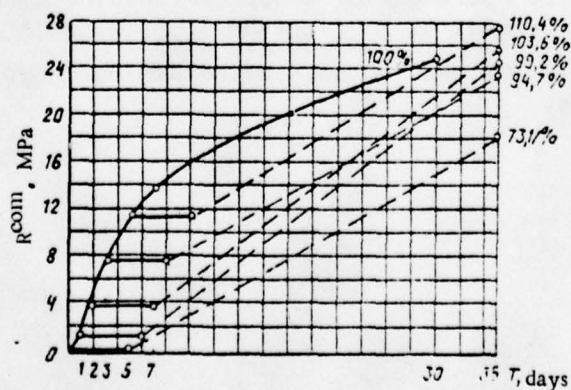


Figure 7.16. Effect of Freezing of Concrete Containing Portland Cement at an Early Age on Subsequent Hardening.



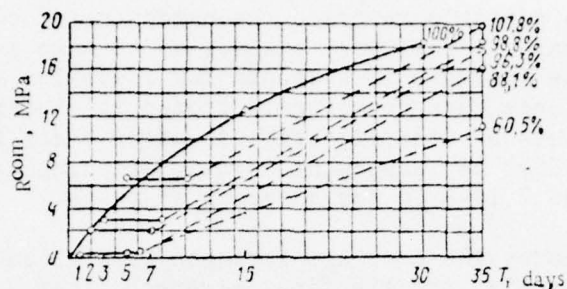


Figure 7.17. Effect of Freezing of Concrete Containing Pozzuolanic Portland Cement at an Early Age on Subsequent Hardening.

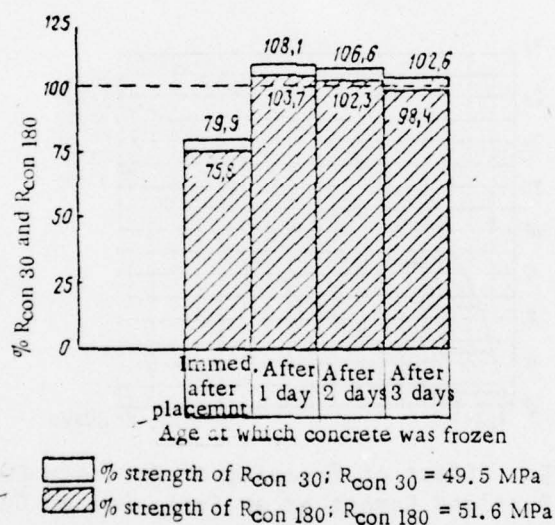


Figure 7.18. Strength of Concrete Containing Bauxite Cement in Percent of  $R_{con 30}$  and  $R_{con 180}$  after Freezing at an Early Age and 180 Days of Hardening Under Normal Conditions.

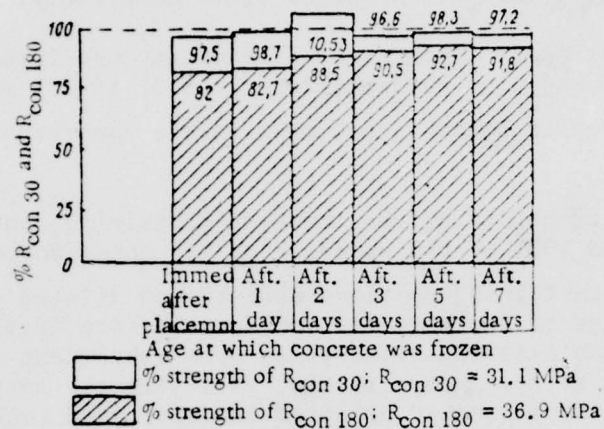


Figure 7.19. Strength of Concrete Containing Portland Cement With an Activity of 45.9 MPa in % of  $R_{con\ 30}$  and  $R_{con\ 180}$  After Freezing at an Early Age and 180 Days of Hardening Under Normal Conditions.

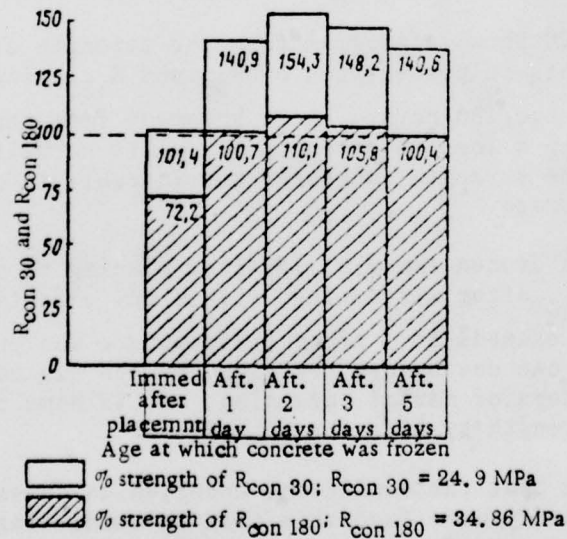


Figure 7.20. Strength of Concrete Containing Portland Cement With an Activity of 42.8 MPa in % of  $R_{con\ 30}$  and  $R_{con\ 180}$  After Freezing at an Early Age and 180 Days of Hardening Under Normal Conditions.

The concrete was placed very compactly and setting of this cement apparently began by the instant the cubes froze completely.

When concrete is frozen soon after preparation the losses in strength after the month of subsequent hardening are from 27 to 47% of  $R_{30}$ . In this case a 30.2% drop in strength occurred in the concrete containing bauxite cement.

After 24 hours of hardening the concrete containing bauxite cement subsequently acquired 102% of the strength of  $R_{30}$  under normal conditions, and concrete containing portland cements and diluted cements from 80 to 99%. As the age of the concrete increases before freezing the percentage of attainable strength increases upon subsequent storage. Freezing of concrete at age 3 days results in a strength loss of no more than 16%. In this case it should be noted that portland cement exhibited a rather high percentage of strength loss.

In all other cases concrete frozen at age 3 days subsequently lost from 2 to 10% of the strength after 27 days in a normal storage chamber. Concrete containing ordinary and mixed portland cements loses a small percentage of its strength even at age 5-7 days before freezing.

Table 7.4 gives the results of tests of concrete containing six different cements after samples were exposed to freezing conditions immediately, 1, 2, 3, 5, 7 and 15 days after preparation and then stored 180 days under normal conditions after 5 days of freezing.

Figures 7.14-7.20 show in diagram form the strength of concrete containing four cements in percentages of  $R_{30}$  and  $R_{180}$  after freezing and normal storage up to age 180 days. As is apparent from these data, freezing of concrete results in a loss in strength vis-a-vis normally hardened samples. However, the strength increased considerably in due course upon subsequent normal storage.

When concrete is frozen immediately after placing it in the forms strength approaches 100% of  $R_{30}$  after six months, with a few exceptions, and in a number of cases even exceeds it. After the concrete was cured under normal conditions more than one day before freezing, by age six months strength was at least that of 30 days of normal hardening, and in some cases exceeded the 30 day normal strength by a factor of 1.5.

It must be noted that the conditions under which these tests were conducted are undoubtedly more favorable than in conducting operations in freezing weather. Repeated freezing, moisture loss by evaporation, moistening during thaws (in a case of precipitation), and loose placement of the concrete in the structure which do occur in practice may result in considerably greater strength losses than occurred in the tests indicated previously.



TABLE 7.4. EFFECT OF 5 DAYS OF FREEZING AND 180 DAYS OF HARDENING UNDER NORMAL CONDITIONS ON THE STRENGTH OF CONCRETE

Cement	Sample strength, % of R <sub>30</sub> , at age, days						
	Immed. after prepar.	1	2	3	5	7	15
Bauxite cement, 50 MPa	80	108	107	103	—	—	—
Portland cement, 46 MPa	98	98	105	97	93	97	—
Portland cement, 42.8 MPa	101	101	154	148	141	—	—
Portland cement, 32.3 MPa	99	117	—	141	140	140	—
Pozzuolanic port- land cement	86	136	146	138	136	129	139

In solving the problem of the suitability of accidentally early frozen structures, we may recommend on the basis of the data cited here as well as many others that the substantial increase in strength of concrete with a passage of a prolonged period of time be taken into consideration. The supportive ability of concrete and reinforced concrete structures can be increased by creating favorable hygrothermal conditions. To do this the dismantling and loading period of the structures should be delayed several months, into spring or even summer. Tests conducted in 1934-1940 using various cements and the most diverse concrete freezing conditions showed that it is preferable to speak of critical strength, not critical age of the concrete before freezing.

#### Effect of Early Freezing on Cohesion of Concrete and Metal Reinforcement.

In our studies we have not limited ourselves to tests of concrete alone. Samples of reinforced concrete were also frozen. Prisms  $10 \times 10 \times 20$  cm in which round steel rods with a diameter of 19 mm were embedded were used as the test samples.

As tests have shown, early freezing of reinforced concrete causes a sharp drop in the cohesion between the metal reinforcement and concrete.

The loss of relative strength in the cohesion of metal and concrete in those cases in which freezing occurs soon after placement of the concrete and vertical positioning of the rods are completed is much greater than the loss of compression strength of concrete. Test data from analyses of concrete containing portland cement and slag portland cement are shown in Figure 7.21 and 7.22.

As can be seen from these figures, freezing of reinforced concrete immediately after placing the concrete containing the two cements later results in almost complete disruption of the metal-concrete bond. For concrete containing portland cement frozen at age 3 days, when more than

30% of the strength of  $R_{28}$  is already ensured, the subsequent cohesion losses are no more significant than concrete compression losses. Much poorer results are obtained in concrete containing slag portland cement.

Accordingly, freezing of reinforced concrete soon after placing the concrete is more harmful than freezing of the concrete itself.

The compression strength loss of concrete after freezing soon after placement and after 3 days and the cohesion loss between the metal and concrete are compared in the figures cited.

Concomitantly with comparing the compression strength of concrete to the reinforcement-concrete bond in a case of early freezing, a test was conducted to determine the tensile bending strength of concrete in prisms. This indicator is even more interesting than compression strength on which a great deal of data have been cited.

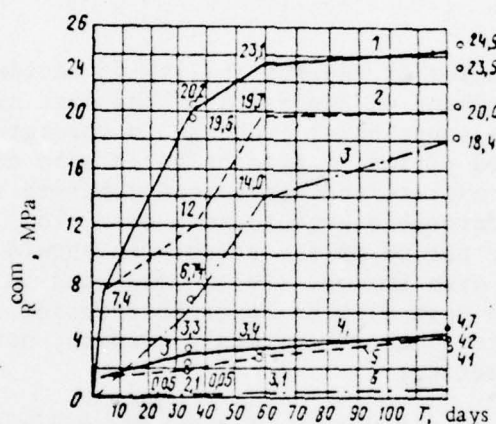


Figure 7.21. Effect of Sub-Zero Temperatures on Concrete-Steel Cohesion (Concrete Containing Grade 500 Portland Cement, Composition by Volume 1:2.2:3.7). 1, Compression strength under normal hardening conditions; 2, Compression strength of samples frozen at age 3 days; 3, Compression strength of samples frozen immediately; 4, Binding strength of control samples; 5, Binding strength of control samples frozen at age 3 days; 6, Binding strength of control samples frozen immediately.

As can be seen from Table 7.5, the strength deficit as the result of early freezing was approximately within the same limits as in determining the compression strength loss of concretes frozen under similar conditions. It should be noted, however, that this test was conducted on concrete containing fresh limestone. When using such aggregates as gravel and crushed granite, the strength deficit increases.

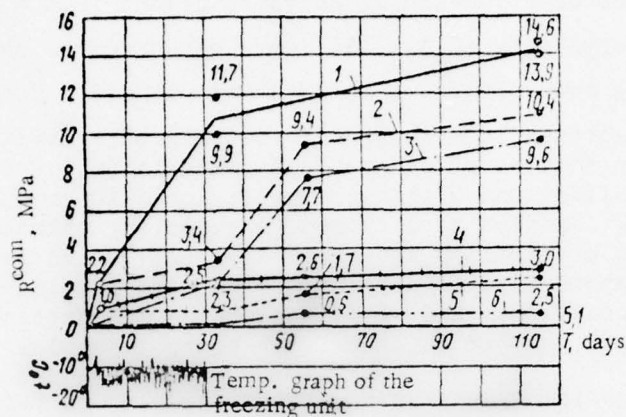


Figure 7.22. Effect of Sub-Zero Temperatures on Concrete-Steel Cohesion (Concrete Containing Slag Portland Cement, Composition by Volume 1:2.2:3.7). 1, Compression strength of normal samples; 2, Compression strength of samples frozen at age 3 days; 3, Compression strength of samples frozen immediately; 4, Binding strength of normal samples; 5, Binding strength of samples frozen at age 3 days; 6, Binding strength of samples frozen immediately.

TABLE 7.5. EFFECT OF PRECURING BEFORE FREEZING ON TENSILE BENDING OF CONCRETE (AT  $t = -20^{\circ}\text{C}$ )

Precuring time before freezing, hours	Tensile bending strength of beams 10 x 10 x 40 cm	
	MPa	% of $R_{28}$
0	1,75	60
6	2,2	77
12	2,5	86
24	2,5	86
72	2,8	96
28 days of normal hardening	2,9	100

Note. Samples cured 3 days in freezing weather and 28 days after thawing under normal conditions.

Commas indicate decimal points.

Hardening of Concrete Containing Various Portland Cements and Aggregates After Freezing at From  $-2$  to  $-50^{\circ}\text{C}$ .

Some results of experimental studies conducted at the Scientific Research Institute of Concrete and Reinforced Concrete from 1957 to 1975 are cited below.



Tests on concretes containing Belgorod cement ( $C_3A = 4\%$ ), Voskresenskiy ( $C_3A = 7\%$ ) and Nevyanskiy ( $C_3A = 13\%$ ) were conducted to show the effect of the mineralogical composition of cements and primarily  $C_3A$  mineral content in them on the increase in strength of concrete after thawing. The tests were conducted on samples of concrete of composition 1:2:3.7 with a  $W/C = 0.58$ . Crushed limestone with a grain size of 5-10 mm was used as the coarse aggregate. Samples were frozen in a cooling chamber at  $-20^\circ C$  immediately after preparation and after 3, 6, 9, 12 and 24 hours of precuring at an above-zero temperature. The test samples remained 3 days under freezing conditions, and were then thawed and hardened 28 days more in a normal storage chamber together with control samples.

TABLE 7.6. EFFECT OF PRECURING BEFORE FREEZING ON THE STRENGTH OF CONCRETE (AT  $t = -20^\circ C$ )

Precuring time, hours	Strength of concrete frozen at an early age and hardened 28 days under normal conditions containing the following cements					
	Belgorod		Voskresenskiy		Nevyanskiy	
	MPa	% of $R_{28}$	MPa	% of $R_{28}$	MPa	% of $R_{28}$
0	22.2	70	20	62	29.7	86
3	20.9	66	22.5	70	27.6	80
6	24.1	76	23	72	38	110
9	26.9	85	26.2	82	37.7	110
12	26	82	28	87.5	41.1	120
14	28.6	90	29.8	93	39.8	115
Normal storage	31.7	100	32	100	34.5	100

Commas indicate decimal points.

As results of these studies have shown (Table 7.6), concretes containing Belgorod and Voskresenskiy cements demonstrate identical strength losses upon freezing at an early age: 30-40% when they are frozen before the completion of cement setting; almost 20% when frozen 9 and 12 hours after preparation and 7-10% when frozen after 24 hours of precuring. Such similar results are due to the minor difference in their mineralogical composition. Although Voskresenskiy cement contains a somewhat larger amount of  $C_3A$ , in return its content of mineral  $C_3S$  which is the principal bearer of strength and also determines concrete hardening at sub-zero temperatures and after thawing is 8% less than in Belgorod cement.

Concrete containing Nevyanskiy cement which is characterized by more rapid hardening in the initial periods and which has the strength of 9 MPa after 24 hours demonstrated considerable losses of strength (approximately 20%) when it was frozen to the completion of setting of the cement. When concrete containing this cement was frozen at age 6 hours, its strength was later the same or higher than in normally hardened samples.

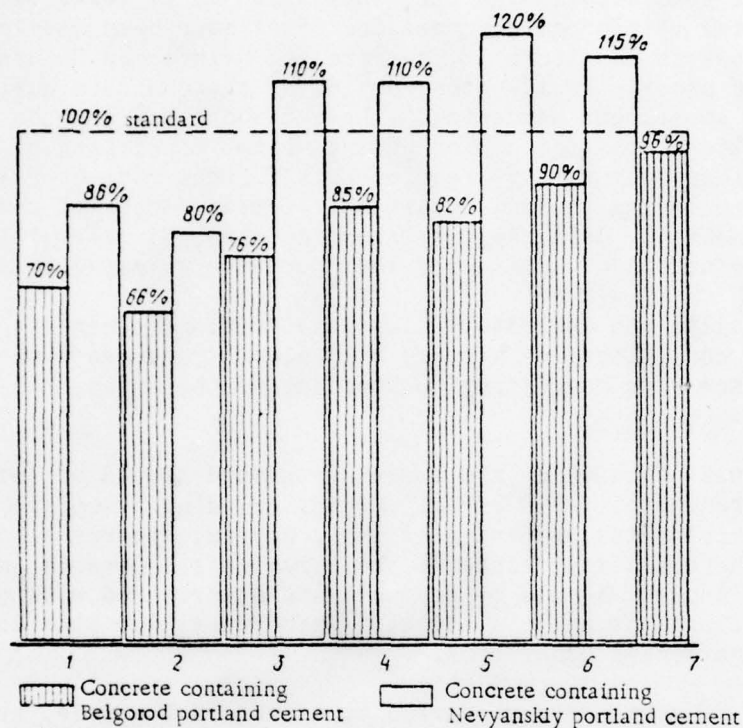


Figure 7.23. Strength of Concrete 28 Days After Thawing (in % of Standard). 1, Frozen immediately after preparation; 2, Frozen 3 hours after preparation; 3, 6 hours; 4, 9 hours; 5, 12 hours; 6, 24 hours; 7, 72 hours.

It is known that cements with an increased  $C_3A$  content are characterized by earlier setting times and greater strength in the initial hardening. This causes fewer structural dislocations and less strength losses later on by concretes containing these cements.

Figure 7.23 graphically shows the results of tests of concrete containing Belgorod and Nevsky cements. As can be seen from the diagram, concrete already frozen 6 hours which contains Nevsky portland cement later acquires strength 10% greater than that rated.

In spite of unfavorable conditions for the hardening of concrete at sub-zero temperatures and at reduced above-zero temperatures in spring-fall, builders must use cements of the same quality as under summer conditions. Moreover, very frequently quick hardening cements are used in prefabricated reinforced concrete factories during thermal treatment, and such cements as slag portland cement and low grade portland cement must be used for winter concreting. Such cements are supplied to remote regions of the North and Far East. This raises the costs of conducting operations and delays the start-up of facilities. Therefore since the 1930's the author has posed the question more than once of the adoption of special cements for thermal treatment and non-thermal methods of winter concreting.

Technical specifications for cements which it is feasible to supply to prefabricated reinforced concrete factories have been developed at the Scientific Research Institute of Concrete and Reinforced Concrete. These cements should provide rapid strengthening of the concrete during thermal treatment and subsequent hardening. These cements may also be successfully used in electrical or steam curing during winter concreting of cast in situ structures. They must satisfy requirements for the rate of gain in strength by the concrete during thermal treatment. Cement factories can satisfy these requirements by using appropriate mineralogical compositions of the clinker, introduction of admixtures and increased grinding fineness.

If high alite and moderately aluminate portland cement is desirable under factory conditions, as a rule, high aluminate cements should be given preference when concreting in freezing weather using non-thermal methods.

The fineness with which the cement is ground should be increased, but only to within approximately  $4000 \text{ cm}^2/\text{g}$ . Higher grinding fineness of the cement, although it accelerates hardening of the concrete, increases contraction and reduces the crack resistance of the structures. Cements in the construction industry should be produced and distributed with consideration of their use not only in specific structures, but also depending on the concrete hardening conditions.

A number of tests were conducted to ascertain the role, type and density of aggregates in freezing concrete at an early age. The results of testing concrete containing the following aggregates are cited below: crushed limestone, granite and brick, expanded shale aggregate and slag pumice.

A constant actual water-cement ratio of 0.65 was adopted for purposes of comparing the results. In this case it was necessary to consider the amount of water absorbed by the coarse aggregates in 30 minutes. The mixture was prepared with a slump of 1-2 cm. Concrete samples  $10 \times 10 \times 10$  cm in metal forms were exposed to freezing conditions at  $t = -5$  and  $-20^\circ\text{C}$ .

By analyzing the data obtained (Table 7.7) we may note that when using porous aggregates the strength of the concrete under normal conditions is 30-40% lower than for dense aggregates. In concrete containing slag pumice the strength indicators are higher than in concrete containing other porous aggregates. In 28 days of normal hardening after freezing, strength losses in concretes containing porous as well as dense aggregates are approximately identical. This is due to the fact that the W/C was assumed to be the same and the aggregates were used in a water saturated state. At  $-5^\circ\text{C}$  the strength losses in concrete containing crushed limestone and slag pumice were greater than at a freezing temperature of  $-20^\circ\text{C}$ . The use of unsaturated porous aggregates before mixing ensures higher strength indicators, frost resistance and other properties. Concrete containing expanded shale aggregate which has the highest water absorption of the aggregates taken (19.1%) exhibited the poorest results under dry air conditions (22% strength loss) and that containing slag pumice with 6% water absorption lost 10% in all. This indicates that more dense light aggregates with a low porosity



and water absorption may be used on an equal footing with dense aggregates in a case of early freezing of concrete. Here a strength which differs little from concretes containing a dense aggregate (29 MPa for concrete containing crushed limestone and 26.7 MPa for concrete containing slag pumice) may be obtained after freezing under dry air conditions.

TABLE 7.7. EFFECT OF AGGREGATES ON THE STRENGTH OF CONCRETE FROZEN AT AN EARLY AGE AND THEN STORED 28 DAYS UNDER DRY AIR CONDITIONS

Aggregate	Strength of the concrete frozen				28 days storage under	
	Immediately after preparation	During setting period, 9 hrs. 35 min. later	24 hrs. normal storage later	24 hrs. dry air storage later	Normal conditions	Dry air conditions
Crushed limestone	29	29,5	36,4	30,5	36	33,5
	80	82	101	85	100	
Crushed granite	29,4	32,2	33,2	31,7	38	32,3
	77	85	88	84	100	
Expanded shale aggregate	22	22,2	23,8	22,6	28,4	26,5
	78	78	84	80	100	
Slag pumice	26,7	26,8	26,5	25,6	29,8	29
	90	90	89	86	100	
Crushed brick	22,4	23,3	23,8	24,8	27	27,1
	83	86	83	92	100	

Note. Numerator indicates strength in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

With regard to 24 hour curing before freezing, it may be noted that it plays no great role [translator's note: next line out of place; it reads: (29 MPa for crushed limestone and 26.7 MPa for slag ...) for dense as well as porous aggregates. However, a number of peculiarities should nevertheless be noted. Firstly, in all cases (but one) curing under dry air conditions is more effective at above-zero temperatures upon subsequent storage. Under normal conditions 24 hour curing for concretes containing crushed limestone (101%) and crushed granite (88%) is especially effective.

Establishing the Critical Strength of Concrete Depending on Temperature, Length of Freezing and Concrete Composition.

A large number of experiments were conducted to establish with some degree of soundness that strength after reaching which concrete frozen at an early age subsequently is able to acquire a given design grade with the onset of warm weather. It was necessary to check what effect is exerted

by such factors as the value and length of the action of a sub-zero temperature, water-cement ratio, water content and length of subsequent hardening of concrete at an above-zero temperature. O. S. Ivanova and Ye. G. Glazyrina participated in these experiments in the laboratory for methods of accelerating the hardening of concrete of the Scientific Research Institute of Concrete and Reinforced Concrete.

Let us first examine the results of the experiment with concrete of composition 1:3.3:4.5 at a W/C = 0.72. The concrete was mixed using grade 500 portland cement from the Novorossiyskiy Factory with a slump of 1-3 cm. Crushed limestone was used as the coarse aggregate in this and the other experiments. Concrete samples  $10 \times 10 \times 10$  cm were frozen at  $-20$  and  $-50^{\circ}\text{C}$  for 1, 7, 28 and 90 days. The samples were thawed and subsequently hardened in a normal storage chamber. Some of them were compression tested after 5-6 hours of thawing.

The second experiment was conducted with concrete of composition 1:1.9:2.8 at a W/C = 0.47. All other parameters were the same as in the first experiment. The results of testing the concrete after curing under set conditions are shown in Tables 7.8 and 7.9.

The results of these experiments were compared with results obtained previously on the freezing of concrete containing grade 400 Yashkinskiy portland cement at  $-10$ ,  $-20$  and  $-50^{\circ}\text{C}$  in Novokuznetsk.

First of all, we must conclude that no substantial difference between samples frozen at  $-20$  and  $-50^{\circ}\text{C}$  was detected. Ordinary variations in the results obtained in either direction occur. Therefore we should examine the individual circumstances associated with the rate of freezing and thawing of the concrete, with the phase changes in the water and possible hydration of the cement upon freezing at different stages of hardening.

Early freezing is equally damaging when concrete is frozen at  $-20$  as well as  $-50^{\circ}\text{C}$ . As has already been shown previously, freezing at the initial stage of hardening is damaging at all sub-zero temperatures. In these tests freezing causes no substantial damage in the structure and in gain of strength upon subsequent hardening after the concrete had reached a strength of 30-40% of  $R_{28}$ . This principal conclusion was used in refining the chapter of the SNIIP III-B.1-70 on winter concreting.

The similarity of the results obtained is due to the fact that the phase state of water was practically identical at each temperature. The rate of freezing of concrete did not significantly affect its quality at a specific level of strength gain.

The basic phase transformations of water occur when the concrete begins to freeze, when the temperature in it drops to  $-3^{\circ}\text{C}$ . Various imperfections in concrete when frozen at  $-20$  and  $-50^{\circ}\text{C}$  in this case could only be due to the varied rate of freezing.

TABLE 7.8. EFFECT OF CONCRETE STRENGTH BEFORE FREEZING AND DEGREES BELOW ZERO ON HARDENING AFTER FREEZING

Age before freezing, hours	Concrete strength before freezing	Concrete strength after freezing and normal hardening at age, days			
		Immed. after freezing	7	28	90

Freezing temperature  $-20^{\circ}\text{C}$

0	—	—	$\frac{22,6}{65}$	$\frac{23,6}{68}$	$\frac{30,8}{88}$
6	$\frac{0,17}{0,5}$	$\frac{0,95}{2,7}$	$\frac{26,2}{75}$	$\frac{23,4}{67}$	$\frac{32,2}{92}$
24	$\frac{10,6}{31}$	$\frac{13,9}{40}$	$\frac{32,8}{94}$	$\frac{37,6}{108}$	$\frac{37,9}{109}$
48	$\frac{19,3}{55}$	$\frac{20,7}{60}$	$\frac{26,2}{75}$	$\frac{37}{106}$	$\frac{43,5}{125}$
72	$\frac{23,6}{68}$	$\frac{24,6}{71}$	—	$\frac{36,2}{104}$	—

Freezing temperature  $-50^{\circ}\text{C}$

0	—	—	$\frac{25,1}{72}$	$\frac{30,9}{89}$	$\frac{35,5}{102}$
6	$\frac{0,18}{0,5}$	$\frac{0,6}{0,18}$	$\frac{24,1}{69}$	$\frac{27,2}{78}$	$\frac{29,9}{86}$
24	$\frac{11,2}{32}$	$\frac{14,7}{42}$	$\frac{30,6}{88}$	$\frac{35,4}{102}$	$\frac{35,8}{103}$

Notes: 1. Numerator indicates strength of concrete in MPa, denominator in % of  $R_{28}$ .

2. Grade of normally hardened concrete 34.8 MPa. Commas indicate decimal points.



TABLE 7.9. EFFECT OF PRECURING BEFORE FREEZING ON THE STRENGTH OF CONCRETE AFTER FREEZING AND NORMAL HARDENING

Time before freezing	Concrete strength <sup>a</sup> before freezing	Concrete strength <sup>a</sup> upon prolonged freezing, days			
		Immed. after thawing	7	28	90
Freezing temperature -20°C					
0	—	—	$\frac{14,4}{60}$	$\frac{18,6}{78}$	—
6 hrs.	$\frac{0,1}{0,4}$	$\frac{0,24}{1}$	$\frac{13,5}{57}$	$\frac{19,7}{83}$	$\frac{20,7}{87}$
	$\frac{0,5}{20}$	$\frac{0,52}{2,2}$	—	$\frac{20,3}{85}$	$\frac{20,4}{86}$
12 hrs.	$\frac{3,4}{14}$	$\frac{4,8}{21}$	$\frac{12,7}{53}$	$\frac{22,6}{95}$	$\frac{20,8}{88}$
	$\frac{8,3}{35}$	$\frac{9,3}{39}$	$\frac{13,3}{56}$	$\frac{21,7}{91}$	$\frac{20,2}{85}$
24 hrs.	$\frac{10,2}{43}$	$\frac{9,9}{42}$	$\frac{13,6}{57}$	$\frac{24}{101}$	$\frac{27,2}{114}$
	$\frac{14,5}{61}$	$\frac{15,9}{67}$	$\frac{18,5}{73}$	$\frac{22,2}{93}$	$\frac{23,2}{97}$
7 days					
Freezing temperature -50°C					
0	0	—	$\frac{4,6}{19}$	$\frac{19,8}{81}$	$\frac{20}{82}$
1 day	$\frac{3,5}{14,4}$	$\frac{6}{25}$	$\frac{10,6}{43}$	$\frac{18,4}{75}$	$\frac{21,8}{90}$
	$\frac{6,5}{27}$	$\frac{7,3}{30}$	$\frac{12,2}{50}$	$\frac{20}{82}$	$\frac{22,7}{94}$
2 days	$\frac{11,65}{48}$	$\frac{12,8}{52}$	$\frac{14,9}{61}$	$\frac{19,3}{79}$	$\frac{23,8}{98}$
	$\frac{14}{58}$	$\frac{15,5}{64}$	$\frac{17,2}{70}$	$\frac{21}{86}$	$\frac{23,9}{98}$
3 days					
4 days					

\*Numerator shows strength of concrete in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

At lower sub-zero temperatures water cannot be redistributed: it migrates from warmer layers of the concrete to colder ones, saturates them and forms water and then ice inclusions and lenses. This is usually observed when concrete is frozen at an extremely early age. As was shown in Chapter 6, sub-zero temperatures near 0°C frequently have a more damaging effect.

The results of a similar test, but with a lower grade concrete, i.e., a composition with a W/C = 0.72, are cited below.

Strength losses amounted to 11 and 18% when the concrete was frozen at -50°C at the earliest age, and 22-32% at -20°C. In almost all cases the concrete achieved a strength of 30-40% of the rated strength of 8-10 MPa which was sufficient to take up tensile stresses which arise when concrete is frozen, and the strength losses in it did not exceed 10%. Freezing of concrete at an earlier age causes strength losses of up to 40% of  $R_{28}$ .

Figure 7.24 shows the results of studies of the effect of a freezing temperature of -5, -20 and -50°C on the gain in strength by concrete upon subsequent hardening under normal conditions up to age 180 days. In this experiment, freezing of concrete after preparation and at age 24 hours was most unfavorable at -20°C.

In work [3] concrete containing two cements was frozen immediately after preparation at -2, -5, -10 and -20°C (Table 7.10). The greatest strength losses (44%) were obtained when samples were frozen at a temperature of -2°C, then at -5°C (38%) and the least at -10 and -20°C (20-25%). The causes of the great losses at higher sub-zero temperatures include the slower cooling of samples and the possibility of moisture migration which creates more favorable conditions for the formation of macro-inclusions of ice which seriously damage the concrete structure and result in considerable strength losses later on.

TABLE 7.10. EFFECT OF FREEZING TEMPERATURE ON THE STRENGTH OF CONCRETE FROZEN IMMEDIATELY AFTER PREPARATION AND HARDENED 28 DAYS AFTER THAWING UNDER NORMAL CONDITIONS

Freezing temperature, °C	Compression strength of concrete containing			
	Belgorod cement and crushed limestone		Voskresenskiy cement and crushed granite	
	MPa	% of $R_{28}$	MPa	% of $R_{28}$
-20	27,9	77	16,9	82
-10	26,9	75	16,4	80
-5	23,3	62	12,9	62
-2	20,1	56	—	—
Normal hardening	35,9	100	20,6	100

Commas indicate decimal points.

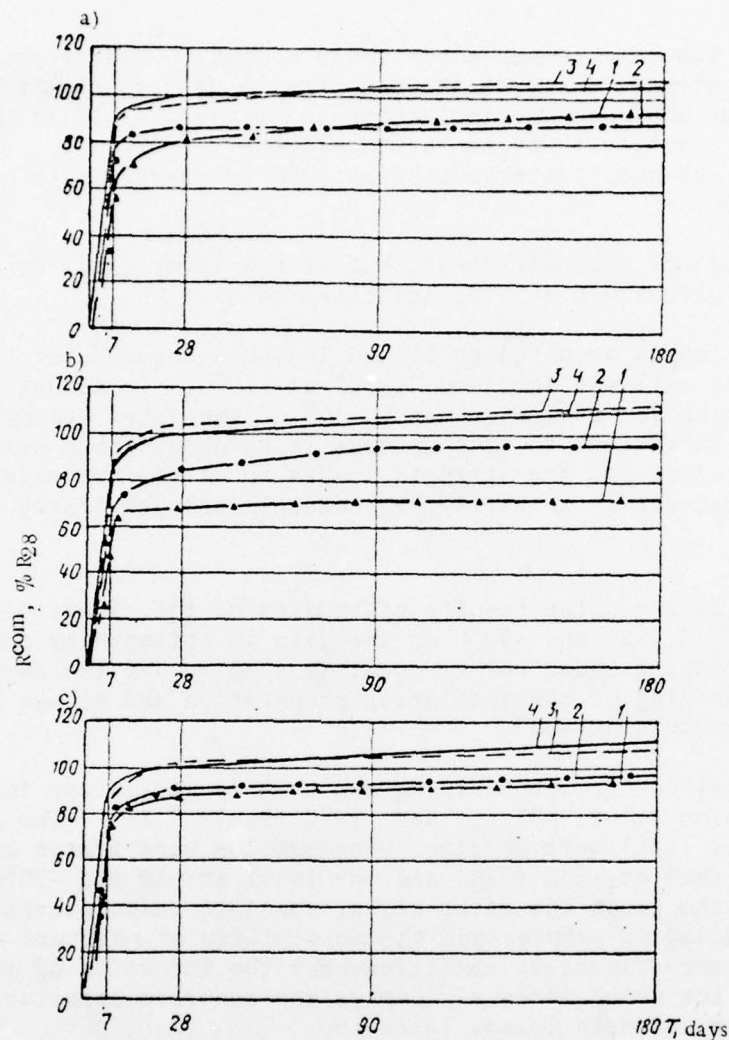


Figure 7.24. Effect of Freezing Temperature and Strength Before Freezing on the Nature of the Increase in Strength After Thawing of Grade 300 Concrete. Freezing temperature: a,  $t = -5^{\circ}\text{C}$ ; b,  $t = -20^{\circ}\text{C}$ ; c,  $t = -50^{\circ}\text{C}$ ; 1, Frozen immediately after preparation; 2, Frozen at a strength of 15-17% of  $R_{28}$ ; 3, At a strength of 28-35% of  $R_{28}$ ; 4, Normal storage conditions.

The effect of freezing at  $-2^{\circ}\text{C}$  on concrete should be especially noted. At from 0 to  $-2^{\circ}\text{C}$  the water in the concrete may remain in the unfrozen state for some time, but all that is necessary is that the temperature be lowered even a few tenths of a degree below  $-2^{\circ}\text{C}$  and it immediately freezes. Some variation in the temperature, both increasing and decreasing, occurred in the cooling chamber with  $t = -2^{\circ}\text{C}$ . Therefore when freezing concrete at  $-2^{\circ}\text{C}$  we often obtained a considerably larger strength deficit than at  $-20^{\circ}\text{C}$ .



It must be noted that different technological factors exerted the most considerable effect on the strength of concrete at various stages of freezing of it (according to its age and strength).

When concrete is frozen at an early age its water content is of greatest significance. With a water content of more than  $180 \text{ kg/m}^3$  the strength losses at age 28 days were as a rule at a maximum. The water-cement ratio plays no significant role when concrete is frozen at an early age (with the same water content).

Thus, for example, for concretes with a water content of  $180 \text{ kg/m}^3$  and a  $W/C = 0.47$  the strength loss after freezing at an early age at  $-20^\circ\text{C}$  was 32%, and at a  $W/C = 0.72$  it was 22% of  $R_{28}$ . At the same time, for concretes with a  $W/C = 0.72$  and a slump of 1-2 cm the strength losses at a water consumption of  $W = 200 \text{ l/m}^3$  reached 40% (at  $180 \text{ l/m}^3 - 22\%$ ), and at  $150 \text{ l/m}^3$  they were 17% of  $R_{28}$  overall. When concrete with a  $W/C = 0.47$  and water consumption of  $155 \text{ l/m}^3$  was frozen at  $-50^\circ\text{C}$  the strength losses did not exceed 18%.

By reducing the water content of the concrete we limit the amount of ice formation, as the result of which destructive processes in the concrete during freezing are reduced and therefore fewer strength losses are obtained at age 28 days. Precuring of concrete for 6 hours, i.e., until it reaches a strength of approximately 0.2-0.3 MPa, changes this situation little. This is not enough to take up the tensile stresses and more deformations and structural damage occur.

When concrete with an initial strength of approximately 15% and higher (of  $R_{28}$ ) is frozen the water-cement ratio is the important factor, since it greatly affects the intensity of gel formation, especially in the initial period of concrete hardening. Intensive accumulation of gel occurs up to the critical strength and the porosity of the concrete changes qualitatively: the capillary porosity, which is especially dangerous during freezing, drops considerably and the gel porosity increases to the same degree. More cement in the concrete considerably accelerates these processes and the free water becomes chemically and physically bound or partially freezes [19, 32].

The initial water content of concrete (water consumption approximately  $180 \text{ l/m}^3$ ) has no substantial effect on the drop in strength during freezing if the concrete has acquired more than 30% of  $R_{28}$  at the instant of freezing. However, at a high water-cement ratio the initial water content of the concrete strongly affects the rates of strength increase before freezing. Thus, for example, at a  $W/C = 0.72$  and  $W = 150 \text{ l/m}^3$  the concrete acquired 30% of the strength of  $R_{28}$  in 24 hours, and at a  $W/C = 0.72$  and  $W = 180$  and  $200 \text{ l/m}^3$  the same only in 48 hours.

The tests described previously were conducted on concretes with an identical mixture consistency. To ascertain the effect of water alone, we prepared a group of concretes with a constant cement consumption of

330 kg/m<sup>3</sup> and an equal water-cement ratio and consequently with varied consistency of the concrete mixture. The water-cement ratio was: 0.45; 0.5; 0.6; 0.7 and 0.8, water consumption and consistency were respectively 150 l/m<sup>3</sup> and 90-120 s; 160 l/m<sup>3</sup> and 50-60 s; 198 l/m<sup>3</sup> and 15-20 s (slump = 3 cm); 232 l/m<sup>3</sup> and slump of 15 cm; 264 l/m<sup>3</sup> where the mixture ran, in spite of the very large amount of sand in it ( $r = 0.45$ ).

The consumption of water at the same cement content exerts a very great effect on the increase in strength of the concrete before freezing as well as on the strength losses of the concrete after freezing.

Concretes with minimum water consumption which comprise the most stiff mixtures exhibit strength losses of up to 11% even when frozen after preparation. As the water content increases strength losses after freezing increase and reach 40% of  $R_{28}$ .

In order to draw more specific and well-founded conclusions concerning the critical strength, it was decided to determine the effect of the length of freezing on concrete of varied strength at -20, -50°C as well as to ascertain the effect of cyclical freezing on these concretes [19].

O. S. Ivanova determined the effect of the length of freezing on concretes of the same compositions containing the same cements and aggregates as in the first two experiments. Samples 10 × 10 × 10 cm were frozen in cooling chambers at -20 and -50°C for 7, 28 and 90 days. Then they were tested immediately after thawing and after 28 days of hardening. Data on the effect of the length of freezing on the strength of concrete are shown in Tables 7.11 and 7.12.

As can be seen from the data of these tables, prolonged curing of concrete in freezing weather resulted in an increase in strength in a number of cases. The increase in strength becomes noticeable after the concrete was exposed to freezing conditions at age 24 and 48 hours. Apparently some intensification of hydration occurs at this stage of hardening.

Samples 10 × 10 × 10 cm of concrete of composition 1:1.9:2.8 with a W/C = 0.48 and cement consumption of 390 kg/m<sup>3</sup>, i.e., the same composition of concrete containing grade 500 Novorossiyskiy cement and of the group of samples containing Yashkinskiy cement, were prepared to study the length of freezing in steam cured concrete.

Samples of the Novorossiyskiy cement were steam cured in accordance with a 2 + 3 + 2 hour and a 2 + 0 + 2 hour system with 2 hours precuring before heating. In the first case the prefreezing strength was 31.5 MPa or 85% of the control on the day following manufacture and steam curing, and in the second group 24.1 MPa or 65% of the control. Samples with this strength were placed in the cooling chamber at -20°C.

The strength of the samples after 24 hours under freezing conditions increased 14-19% in both groups. However, a longer period of time under

freezing conditions had a varied effect on the samples. The strength of samples from the first group with an initial strength of 31.5 MPa after 90 days of freezing continued to increase and was 141% of the strength of control samples at age 28 days of normal hardening. The strength of samples from the second group with a strength of 65% of  $R_{28}$  gradually decreased as the length of time at  $-20^{\circ}\text{C}$  increased and dropped almost 20% after 90 days of freezing compared to 1 day of freezing. The same occurred upon prolonged freezing of steam cured samples at  $-50^{\circ}\text{C}$  which were made from Yashkinskiy cement in the Novokuznetsk Branch of the Ural Scientific Research Institute of Concrete and Reinforced Concrete.

TABLE 7.11. EFFECT OF THE LENGTH OF CURING OF CONCRETE AT  $-20^{\circ}\text{C}$  ON CONCRETE STRENGTH (CONCRETE COMPOSITION 1:1.9:2.8, W/C = 0.48, W = 186  $\text{g}/\text{m}^3$ ,  $R_{28} = 34.6$  MPa)

Concrete age before freezing, days	Concrete strength <sup>a</sup> before freezing	Concrete strength <sup>a</sup> upon prolonged freezing, days					
		7		28		90	
		Immediately after thawing	28 days of normal harden.	Immed. after thawing	28 days of normal hardening	Immed. after thawing	28 days of normal hardening
1	5.1	8.7	33.8	11.7	31.4	14.2	32.4
	15	25	98	34	91	41	94
2	14.6	18.3	34.2	17.8	34.8	20.4	27.5
	42	53	99	52	100	59	80
3	20.5	22.2	39.8	25	33.5	22.5	32.3
	60	64	115	72	97	65	93
7	25.3	29.4	38	23.3	32.4	24.2	32.2
	73	85	110	67	94	70	93
28	34.6	36.5	—	33.2	—	29.5	—
	100	105	—	96	—	85	—

\*Numerator indicates strength of concrete in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

Let us cite the results of an experiment in determining the effect of precuring before freezing on the strength subsequently attained by concrete at an above-zero temperature for concretes of grades 100, 200, 300, 400 and 500. In this case the concretes were mixed using two portland cements, grade 500 from the Belgorod and Novo-Zdolbunovskiy Factories, the slump of the mixture was the same, 3-4 cm; the water-cement ratio and the cement consumption varied.

Sample cubes  $10 \times 10 \times 10$  cm were frozen in a cooling chamber at  $-15^{\circ}\text{C}$  for 3 days. Preliminary curing and subsequent hardening after freezing were effected in a normal storage chamber ( $t = 20^{\circ}$  and  $W = 90-100\%$ ). The control samples were hardened 28 days under normal conditions.



TABLE 7.12. EFFECT OF THE LENGTH OF FREEZING OF CONCRETE AT  $-50^{\circ}\text{C}$  ON THE STRENGTH OF THE CONCRETE (CONCRETE COMPOSITION 1:1.9:2.8,  $W/C = 0.48$ ,  $W = 186 \text{ l/m}^3$ ,  $R_{28} = 34.6 \text{ MPa}$ )

Concrete curing before freezing, days	Concrete strength <sup>a</sup> before freezing	Concrete strength <sup>a</sup> upon prolonged freezing, days							
		Immed. after thawing	7			Immed. after thawing	28		
			Normal storage conditions, days				Normal hardening conditions, days		
			1	7	28		1	7	28
0	0	0	6.7 31	16.7 77	16.4 76	—	—	—	—
1	3.9	6.6	11.5	20.5	24	8.1	11.7	19.1	22.6
	18	30	53	94	110	37	54	88	104
2	6.8	7	9.4	16.7	21.6	11.8	14.7	20.3	24.1
	31	32	43	77	100	54	68	94	110
3	10.5	12.4	13.8	20.8	21.3	12.9	14.6	21.2	25.2
	49	57	64	96	98	59	68	98	116
4	15	15.8	19.5	22	22.2	15	17.2	22.6	20.3
	69	73	90	102	102	69	79	104	92

\*Numerator indicates strength of concrete in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

TABLE 7.13. EFFECT OF ATTAINABLE STRENGTH BEFORE FREEZING ON ITS SUBSEQUENT INCREASE IN CONCRETES OF VARIOUS GRADES AT AN ABOVE-ZERO TEMPERATURE

Curing time before freezing, days	Concrete strength depending on concrete grade					
	100	150	200	300	400	500
0	100	96	87	85	83	80
	0	0	0	0	0	0
1	84	85	86	89	90	91
	17	18	20	24	26	27
2	87	88	90	92	95	96
	32	33	35	37	44	46
3	90	91	95	97	98	98
	45	46	48	52	55	57
5	100	105	99	97	100	99
	55	58	60	69	71	73
7	99	100	105	100	99	100
	67	65	70	80	84	85
28 (control)	100	100	100	100	100	100

Note. Numerator indicates strength of concrete after 3 days of freezing at  $t = -15^{\circ}\text{C}$  and subsequent 28 day hardening at

an above-zero temperature (under normal conditions), denominator indicates strength of concrete before freezing in %.

Table 7.13 shows mean data on concretes of various grades. It can be seen from these data that concrete of grades 100-150 reaches 95-100% strength with a 5 day precuring period, i.e., with a strength of almost 50% of  $R_{28}$ . Concrete of grades 200-300 acquired this strength in 3 days and has a prefreezing strength in this case of almost 40%. Concretes with higher strength, grades 400 and 500, lose practically no strength later on after 2 days of curing.

The table cites data on the strength of concrete in percentages of that cured before freezing as well as for its subsequent hardening under normal conditions. The indicated grades of concrete were produced, as a rule, with some excess. Results of this conclusive experiment were used together with other experimental data to establish the so-called "critical strength".

#### Effect of Early Freezing on the Properties of Light Concretes.

Requirements for lightening of reinforced concrete structures increase in conjunction with the construction of larger industrial buildings and facilities. The construction of industrial buildings is planned over long periods of time. The use of typical reinforced concrete structures is 20% more economical than metallic structures, and moreover they are considerably more fireproof. Structures of optimum and the most varied forms and sizes can be erected from cast in situ reinforced concrete. Therefore structures of light concretes are attracting more and more attention. The use of light concretes makes it possible to lighten the weight of the buildings up to 30%. It is economical to build such structures as girders, beams, capsules and so forth from light concrete for industrial buildings of large enterprises with a flexible technological system. Their use in cast in situ concrete is continually growing.

In the USSR light concretes have been used most widely in prefabricated industrial construction and especially in supporting structures. In 1973, 20 million cubic meters of reinforced and non-reinforced structures and articles of light concretes were used in construction. In the future the use of light concretes will increase considerably more rapidly than that of normal concretes.

In the Ninth Five-Year Plan, more than 300 plants for light concrete articles and structures located in various regions of the country are operating in the USSR. Artificial porous aggregates were produced at 250 factories which manufactured approximately 20 million cubic meters of gravel, crushed stone, and sand. There are large deposits of natural porous rocks in the Caucasus, the Far East, and on the Kolskiy Peninsula.

The development of production of haydite, ash gravel, schungizite, agloporite, perlite, slag pumice, etc. is planned. In the future, light concretes will be among the most important materials in construction.

In conjunction with this, interest in the study of the properties of light concretes frozen at an early age has grown. Light porous aggregate exhibits a number of special features in comparison with dense aggregates, therefore its role during freezing is somewhat different.

Among the special features of porous aggregate is its bonding strength to cement mortar which is greater than for dense rock. This is due to the fact that when using a porous aggregate its interaction with the binder is intensified by the highly developed contact surface and increased adhesive ability.

Another feature of porous aggregate is its adsorption ability; therefore the structure of the contact layer is formed under conditions of migration of the liquid phase through it due to the existence of moisture and concentration gradients on each side of it. Movement of the liquid phase on the boundary with the porous aggregate was noted in the works of M. Z. Simonov [52].

When mixing concrete the absorption of water begins immediately after immersing the aggregate into the cement paste and it continues mainly throughout the cement setting period. After approximately 24 hours of hardening a slow drop in the content of liquid phase in the aggregate grain is observed; this is due to its counter migration (from the aggregate to the cement stone) by the action of the moisture gradient which arises on contact and also by the chemical binding of water during the cement hydration. This counter-movement of the liquid phase from the aggregate to the cement stone is accelerated more greatly the lower the humidity of the air in which the concrete is located. Subsequent moistening or water saturation of the concrete again causes the liquid phase to move from the cement stone into the aggregate grain.

This property of porous aggregate is of great importance at sub-zero temperatures. The liquid phase which is absorbed by the aggregate up to the time the sub-zero temperature takes effect creates favorable conditions for the formation of a contact zone between the mortar and coarse aggregate. Upon subsequent hardening after thawing the liquid phase is drawn from the aggregate into the cement mortar by the action of the moisture gradient, thus promoting cement hydration in the contact layer. This behavior of the light aggregate during freezing was noted in particular by P. Nernst [46], who pointed out that due to its considerable size the aggregate affects the non-uniform distribution of temperature which in turn affects the direction of movement of the liquid phase. He also noted that grains of large aggregate may serve as low temperature points which will draw off water from the unfrozen paste in all directions and thus create the possibility of the formation of rather thick layers of ice at the early stages of hardening.

It should be noted that the special features of the behavior of light coarse aggregates have not been thoroughly studied in a case of freezing. The effect of aggregate on ice formation and on the dependency of concrete properties in general when it is frozen has been poorly treated.



In order to ascertain the effectiveness of using light concretes containing porous aggregates during winter concreting, their physical-mechanical properties have been studied at the Scientific Research Institute of Concrete and Reinforced Concrete: tensile bending and compression bending strength, deformability, dynamic modulus of elasticity and frost resistance. The following were used as light aggregates in the tests: haydite, agloporite, volcanic slag from the Karmrashenskiy deposits, stony pumice, slag pumice, crushed brick and for purposes of comparison crushed stone of dense rock -- granite and limestone. The portland cements used were from the Belgorod and Novo-Zdolbunovskiy Factories, grades 400-500. The test samples consisted of cubes  $10 \times 10 \times 10$  cm and prisms  $7 \times 7 \times 7$  cm and  $10 \times 10 \times 40$  cm. The test samples were frozen in cooling chambers at -2, -5, -15 and -20°C. The samples were placed in the cooling chambers immediately after preparation and after 1, 3, and 5 days of normal hardening. After 3, 7 or 28 days under freezing conditions the concrete samples were cured in a normal hardening chamber.

Our works in conjunction with those of M. O. Saakyan [34] conducted at the Scientific Research Institute of Concrete and Reinforced Concrete in 1966-1969 devoted special attention to the question of the effectiveness of using light porous aggregates. Concretes containing natural porous aggregates from Armenia (volcanic slag, stony pumice and tuff) were studied in detail in these works. The concrete samples were exposed to the action of sub-zero temperatures of -2, -5 and -20°C and then the increase in strength was determined at sub-zero temperatures and upon subsequent hardening under normal conditions. It was established that at -2 and -5°C, concrete acquires strength rather intensively and practically no loss of it is observed upon subsequent curing at above-zero temperatures. The freezing of concrete containing Karmrashenskiy volcanic slag even immediately after preparation does not cause, as a rule, a strength deficit later on (Figure 7.25). The concrete grade was always guaranteed upon subsequent 28 day hardening under normal conditions. Grades 100-150 concretes exhibited approximately 5%, and grades 200-300 approximately 10% strength deficit only in those cases in which the concrete was frozen immediately after preparation. Samples frozen immediately frequently acquired later on a strength higher than that of samples frozen at age 1 day.

The tensile bending strength after freezing of concrete at -5 and -15°C was studied along with the compression strength of concrete containing Karmrashenskiy slag. In this case a 5-10% strength deficit is noted later on (Table 7.14). The tensile bending strength indicators for concrete containing volcanic slag and expanded shale aggregate after freezing at an early age were subsequently higher than the values required by SNiP II-V.1-62 for normal concretes of corresponding grades.

It should be noted that in spite of the tensile strength values of light concretes exceeding the Construction Norms and Regulations, it was nonetheless lower than in concrete containing limestone aggregate.

TABLE 7.14. TENSILE BENDING STRENGTH OF CONCRETE CONTAINING VARIOUS AGGREGATES AFTER 3 DAYS OF FREEZING AND 28 DAYS OF NORMAL HARDENING

Curing time before freezing, days		Tensile strength of lightweight aggregate concrete*						Tensile strength of conc.* contain. volcanic slag				Tensile strength of normal concrete*			
		Concrete grade													
		75		150		300		50		300		150		300	
		Freezing temperature, °C													
		-5	-15	-5	-15	-5	-15	-5	-15	-5	-15	-5	-15	-5	-15
0	2.9	1.9	2.4	3	3.6	4	1.7	1.9	3.6	3.8	3.3	4	3.4	4	
	95	90	83	94	94	95	90	95	95	93	77	87	70	77	
1	2.33	1.7	2.9	2.9	3.4	4.6	1.8	1.8	3.5	3.8	4.5	4.3	4.6	5	
	90	80	94	91	92	109	92	90	93	94	104	94	93	96	
3	2.4	2.3	3	3.9	3	3	2	1.9	3.64	2.8	4.3	4.5	4.9	5.1	
	104	110	97	103	90	94	100	95	97	93	100	98	100	98	
5	2.4	2.3	3.5	3.4	3.7	4.1	2	2.2	—	—	4.3	4.5	4.95	5.2	
	104	110	113	106	98	97	101	102	—	—	100	98	101	100	
Control, unfrozen (R <sub>28</sub> )	2.3	2.1	3.1	3.2	3.8	4.2	1.9	2	3.8	4	4.3	4.6	4.9	5.2	
	100	100	100	100	100	100	100	100	100	100	100	100	100	100	

\*Numerator indicates strength in MPa, denominator in % of R<sub>28</sub>.

Commas indicate decimal points.



Figure 7.25. Increase in the Strength of Grade 150 Concrete Containing Grade 500 Portland Cement and Volcanic Slag After Freezing at: a,  $t = -5^\circ\text{C}$ ; b,  $t = -20^\circ\text{C}$ ; 1, Storage under normal conditions; 2, Storage in a cooling chamber.

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On the basis of our studies, recommendations were made concerning the feasibility of using natural porous aggregates in Armenia in the concreting of cast in situ structures in cold weather (as is well known, the temperature is often below  $-15 \dots -20^{\circ}\text{C}$  in winter in Armenia, not only in mountainous regions, but in Yerevan itself).

A great deal of research was conducted on the study of properties of concrete containing crushed agloporite frozen at an early age. These studies were associated with building a covered marketplace in Minsk. The cast in situ structures and large covering were designed to be built from high-strength agloporite concrete.

At the Scientific Research Institute of Concrete and Reinforced Concrete, Ye. G. Glazyrina and the author [39] studied deformations, strength and frost resistance of agloporite concrete of various grades. For purposes of comparison, concrete samples containing crushed granite were prepared and frozen at the same time. Quartz sand was used as the fine aggregate to guarantee the required concrete grades. 70% by volume crushed agloporite was consumed. Grade 400 portland cement from the Belgorod Factory was also used. The concrete was mixed to a stiffness of 20-30 s. The mixture was placed in metallic forms and additional weight of  $50 \text{ g/cm}^2$  was used during vibration.

As Table 7.15 shows, grades 150-250 concrete frozen immediately after preparation lose approximately 10% of their possible strength, and that of grades 400-500 approximately 15%.

24 hour curing of concrete before freezing later on ensures complete acquisition of the rated strength.

60 day curing after 3 day freezing of concretes of grades 150-300 ensures 100% of the design strength in all cases. In this case a deficit of from 1 to 8% of the rated strength is noted in grade 400-500 concretes. Here the largest percentage is attributed to grades 400-500 concretes frozen at age 3 days. This strength deficit is apparently due to a spontaneous drop which is often observed, especially in high grade and thermally treated concretes.

This same thing was noted previously in a number of cases; freezing at  $-5^{\circ}\text{C}$  is more damaging to concrete than freezing at  $-20^{\circ}\text{C}$  (Table 7.16). Except for grade 150, concretes of higher grades frozen immediately after preparation exhibited a strength deficit of from 16 to 25% later on upon 28 day hardening under normal conditions. Under longer normal storage, up to 60 days, the losses dropped to 3-9%. When frozen at age 24 hours, 28 day losses still reached 15%. In this case by age 60 days we may assume the concrete has reached its full set rated strength.

On the basis of these studies we may conclude that upon early freezing the strength deficit of agloporite concrete is the same as in concrete containing crushed limestone of corresponding grades and less than in concrete containing crushed granite.

TABLE 7.15. EFFECT OF PREFREEZING CURING ON THE STRENGTH OF AGLOPORITE CONCRETE AFTER 28 AND 60 DAYS OF STORAGE UNDER NORMAL CONDITIONS

Curing time before freezing, days	Strength* at age 28 days after 3 days of freezing at -20°C and grade of concrete					Curing time before freezing, days	Strength* at age 60 days after 3 days of freezing at -20°C and grade of concrete				
	150	250	300	400	500		150	250	300	400	500
0	15.7 90	26.2 98	29.2 89	33.2 87	36.9 84	0	18.1 101	30.2 115	34 101	39.6 99	41.8 96
1	17 97	26 97	33.5 102	40.8 107	43.8 100	1	17.8 100	28.4 106	32.4 99	39.4 98	43.8 100
3	16.9 97	27.3 103	31.5 96	36.4 95	45.9 105	3	20.5 115	32.3 120	36.5 112	36.8 92	42.1 96
Control (unfrozen)	17.5 100	26.8 100	32.7 100	38.1 100	43.6 100	Control (unfrozen)	22 124	29.4 110	36 110	42.4 106	44 101

\*Numerator shows strength in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

TABLE 7.16. EFFECT OF CURING BEFORE FREEZING ON THE STRENGTH OF CONCRETE AFTER 28 AND 60 DAYS STORAGE UNDER NORMAL CONDITIONS DEPENDING ON THE CONCRETE GRADE

Curing time before freezing, days	Strength* at age 28 days after 3 days of freezing at -5°C and grade of concrete					Curing time before freezing, days	Strength* at age 60 days after 3 days of freezing at -5°C and grade of concrete				
	150	250	300	400	500		150	250	300	400	500
0	16.9 95	24 84	27.9 83	30.4 75	35.6 81	0	18.1 102	—	26.9 91	37.7 93	41.4 94
1	17.1 96	27.1 95	33 99	34.4 85	41 94	1	21.5 121	—	35.4 120	38.5 95	43.8 99
3	18.8 106	28.1 98	34 101	39.3 97	44.8 101	3	21.6 122	—	32.2 109	40.1 99	40 91
Control (unfrozen)	17.8 100	28.7 100	33.5 100	40.5 100	44 100	Control (unfrozen)	20 112	—	32.7 110	41 101	45.6 104

\*Numerator shows strength in MPa, denominator in % of  $R_{28}$ .

Commas indicate decimal points.

Precuring of agloporite concrete for more than a few days before freezing later on guaranteed that it acquires the full design strength.

Tests have shown that the less coarse aggregate contained by high strength concrete, the less the compression bending and tensile bending strength losses due to freezing at an early age.

On the basis of these studies, the use of agloporite concrete may be recommended for winter concreting with greater success than ordinary concrete.

We may make a number of generalizations concerning the effect of freezing on light concretes. The compression strength losses of light concretes of grades 50-150 frozen immediately as well as cured before freezing are less than in normal concretes.

Results of testing concretes of grades 200-300 containing porous aggregates exhibit somewhat superior results upon immediate freezing, however the application of preliminary curing compares them with normal concretes.

In analyzing the data obtained in a bending test of concretes containing various aggregates it should first be noted that the absolute values of tensile bending strength of concretes containing crushed limestone are much greater than the values cited in the SNiP: for grade 150 normal concretes 40% higher, and for grade 300 20%. This is due to the use of porous crushed limestone with a porosity of 15% which exhibits a high level of mechanical binding and exerts somewhat of a "reinforcing" effect in concrete.

In concretes containing light porous aggregates the tensile bending strength is greater than the values indicated in SNiP II-V.1-62 for normal concretes; as the grade of the concrete increases this difference drops. In a case of light concretes exposed to sub-zero temperatures immediately after preparation, they lose 5-10% of their tensile bending strength. This is even less than the compression strength losses which amount to 5 to 23%. In a number of cases, freezing at  $-5^{\circ}\text{C}$  reduced the tensile strength of concretes more considerably than freezing at  $-15^{\circ}\text{C}$ . This phenomenon was especially marked in strong concretes.

Just as in compression testing, concretes containing light porous aggregates lose less tensile bending strength as the result of freezing immediately after preparation in concretes containing crushed limestone (13-30%). It has been established that when working with bending material structural defects occur to a greater extent; therefore the insignificant losses in tensile bending strength by light concretes as the result of early freezing prove that their structure is less subject to damage compared to the structure of normal concretes.

A coarse aggregate with a large modulus of elasticity is deformed to a lesser degree, causing overstress of individual portions of the mortar, and it is therefore a concentrator of stresses. As the modulus of elasticity of the coarse aggregate drops, the concentration of stresses in



the concrete drops; this occurs when using light porous aggregate. In contrast to concrete containing a dense aggregate, due to increased cohesion the aggregate in a light concrete is massively bound to the mortar component and forms a unified whole with it; this also increases the mechanical homogeneity of the system. Pores in light aggregates are vessels into which a considerable portion of the mixing water passes in the initial period as well as during the freezing process. The actual W/C drops and the binding of the mortar portion with the coarse aggregate is improved.

The aggregate is compressed by the expanding mortar when using a light porous aggregate due to its relatively low modulus of elasticity: this reduces stress in the concrete. It is apparent from the data obtained on the dynamic modulus of elasticity that the drop in this indicator after freezing for light concretes is 5-10%, whereas it is 24-28% for a normal concrete. The drop in the modulus of elasticity at  $-5^{\circ}\text{C}$  is somewhat greater than at  $-15^{\circ}\text{C}$  for normal as well as light concretes. When concrete is precured before freezing, its modulus of elasticity remains, as a rule, at the same level as concrete frozen immediately. If normal concretes are used, precuring before freezing considerably increases the modulus of elasticity of the concrete, rising mainly for 24 hours of curing (approximately 20%). Upon subsequent curing a small gradual increase in the modulus occurs (2-5%). Thus, in a case of immediate freezing these determinations of the dynamic modulus of elasticity and tensile bending strength have confirmed the advantages of concretes containing light porous aggregates over normal dense concretes.

The frost resistance of concretes frozen at an early age and hardened 28 days under normal conditions was compared to the frost resistance of samples of the same composition under normal storage. Grade 75 lightweight aggregate concrete exhibits a frost resistance factor of 0.85 after 50-100 freezing and thawing cycles, whereas only 35 freezing and thawing cycles are needed for grade 75 structural-thermal insulation concrete according to the "Instructions for Manufacturing Articles of Lightweight Aggregate Concrete". Tests have shown that the frost resistance of light concrete frozen at an early age is greater than the frost resistance of normal concrete of similar grade hardened under the same conditions. This indicates that the structural dislocations caused by the action of the sub-zero temperature are less when using light concrete than when using normal concrete.

Thus, the results of the studies have shown that the losses in compression bending and tensile bending strength as well as the drop in dynamic modulus of elasticity of light concretes frozen immediately after preparation are less than in heavy concretes containing even a porous crushed limestone. Thus, we are able to recommend the wide usage of light porous natural and artificial aggregates for winter concreting.

Consequently, we may recommend not only that builders not hesitate to use concretes containing light porous aggregates in cast in situ structures in winter, but that they are preferable to normal concretes. In this case use of grades 50-150 ( $E_z > E_{\text{tens}}$ ) is more effective in winter concreting:

if necessary, this makes it possible to allow earlier freezing of these concretes. If it is possible to obtain this combination of elastic properties of components in concretes of higher grades, the effectiveness of these compositions for winter concreting will increase.

In winter concreting the requirements for critical strength of low grade, light concretes vary considerably, since after freezing at an early age they acquire full rated strength later on upon 28-90 day storage under normal conditions.

By the instant of freezing of grades 200-400 light concretes the critical strength should satisfy similar requirements for ordinary concretes.